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A HANDBOOK

OF

COLLOID-CHEMISTRY

OSTWALD

Tho. Graham

A HANDBOOK
OF
COLLOID-CHEMISTRY

THE RECOGNITION OF COLLOIDS, THE THEORY OF COLLOIDS, AND THEIR GENERAL PHYSICO-CHEMICAL PROPERTIES

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SECOND ENGLISH EDITION
TRANSLATED FROM THE THIRD GERMAN EDITION

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WITH 63 ILLUSTRATIONS

PHILADELPHIA
P. BLAKISTON'S SON & CO.
1012 WALNUT STREET

21748iB

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THE MAPLE PRESS YORK PA

PREFACE TO THE SECOND EDITION

Yielding to pressure from the publishers who find need at this time for a new printing of this volume, we have reluctantly met their request to revise and bring up to date the original translation as made by the one of us with the assistance of Ralph E. Oesper and Louis Berman. To make such revision when the author of the volume is alive in another country constitutes a delicate if not impossible task. We have met the situation by leaving entirely untouched those large portions of the volume which contain the author's individual views.

Some errors in quotation and in mathematical formulæ as present in the original text have been corrected. Beyond this, one of us (Hatschek) has added numerous paragraphs intended to bring to the reader various important advances in colloid-chemistry which have been made since 1912, especially such as have to do with the mechanical properties of colloids, more particularly their viscosity.

MARTIN H. FISCHER.
EMIL HATSCHEK.

CINCINNATI AND LONDON.
June, 1918.

TRANSLATOR'S PREFACE TO THE FIRST EDITION

The day is past when the importance of colloid-chemistry to the worker in the abstract or applied branches of science needs emphasis. The endeavor of the "pure" chemist to reduce all substances to crystalloid form and from the knowledge of their behavior to resynthesize the phenomena of nature has been a good one, but the limitations of such a point of view have grown daily more apparent. It happens that nature has chosen the colloid form in which to show her face. Crystalloid behavior is the exception, colloid behavior the rule, in the cosmos. Whether we deal with the regions above the earth, as the color of sky, the formation of fogs, the precipitation of rain and snow, or with the earth itself in its muddied streams, its minerals and its soils, or with the molten materials that lie under the earth, the problems of colloid-chemistry are more to the fore than have ever been the crystalloid ones.

To the abstract thinker in science colloid-chemistry therefore, because of its universality, represents the larger field. But the practical worker knows, too, that in a better knowledge of the properties of those very materials which the orthodox chemist has too often cast aside in his jellies, pastes and glues, is found the explanation of so much that interests him. Is it any wonder then that colloid-chemistry appeals to the agriculturalist, the metallurgist, the dealer in precious stones, the tanner of skins, the manufacturer of wood pulps and paper, the dyer, the histologist, the steel worker, the weaver of textiles, the smelter, the manufacturer of paints?

Not only the inorganic world but the organic also has chosen the colloid realm in which to manifest itself. Living matter, whether of plants or animals, and under normal or pathological conditions, is chemistry in a colloid matrix; whence colloid-chemistry comes to concern every botanist and zoologist, the physiologist, the pathologist and the practical man in medicine and surgery.

Under the circumstances, does this volume, known the world over as the authoritative and classical text, need an introduction to any of our people who think in the day's work? It can only seem somewhat strange that three large German editions and seven years were required before its first issue in the tongue of Thomas Graham and the brilliant modern group of English-speaking colloid-chemists. Wolfgang Ostwald's writings represent in colloid-chemistry what those of Charles Gerhardt represent in organic, Justus Liebig in agricultural, and Wilhelm Ostwald in physical chemistry.

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June, 1915.

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PRACTICAL INTRODUCTION

§1. Identification of Colloid Systems by Elementary Methods

(The Elements of Qualitative Colloid-chemical Analysis)

1. General Considerations.—The teachings of colloid-chemistry are by no means so familiar to all who encounter colloid substances in their scientific or practical work that the questions: "How can we recognize a colloid?" or "When is a body said to be a colloid?" are no longer raised. These questions have often been put to me, not only by such men of science as physicists, physical chemists, physicians and mineralogists, but by technologists who for years perhaps have worked exclusively in such practical colloid problems as the manufacture of rubber. Even the organic and inorganic chemists frequently encounter phenomena, particularly when they work with highly polymerized and highly complex substances that remind them of what they know of the properties of colloids, and make them ask how they can determine quickly and simply whether colloid-chemical principles will help them in the solution of their problem or no. As a matter of fact I am of the opinion that such questions have not been asked frequently enough, say in organic chemistry, where examination of the colloid behavior of one and the same organic substance in different solvents would throw much light on the properties observed.[1] The youth of colloid-chemistry itself justifies such questions, and their discussion is by no means either useless or superfluous.

An answer to the question: "How do we know when we are dealing with a colloid?" would consist in a presentation of the elementary properties and the experimentally observed behavior of colloid substances. Such an analysis would constitute *the elements of a qualitative colloid-chemical analysis.* A possible method of procedure in attempting to discover the colloid nature of any substance is indicated in the following:

---

[1] We need but call to mind the modern problem of the relation to each other, in solvents of various kinds, of color, chemical constitution, and molecular state as studied by A. Hantzsch and his pupils. It seems to me that a colloid-chemical (dialytic or ultramicroscopic) examination of such variously colored solutions would bring light especially in those cases in which molecular weight determinations have been exhausted without result. The failure of Beer's law governing the proportionality between thickness of layer and light absorption when applied to colloids and to solutions of dyes, oxime salts and organic ammonium salts as well as other facts seem to me to indicate that suitable colloid-chemical investigations in this field will bring to light as surprising facts as did those of J. Amann (Koll.-Zeitschr., **6**, 235, **7**, 67 (1910)) on the colloid and molecular solubility of iodine in various solvents.

2. The Colloid State is Independent of Chemical Composition.—At first sight one might hope to obtain an answer to the question under consideration by constructing a comprehensive *table of all the colloid substances or groups of substances known.* As a matter of fact such attempts[1] have been made even recently, but never with the full approval of competent workers in the field. It was soon noticed that we cannot speak of colloid substances in the same way as we (still) do of "liquid-crystalline" or "radio-active" substances. We have been compelled to recognize that colloid properties are in no way connected with any particular type of chemical constitution to the end that only certain elements or certain compounds, for example, appear as colloids. We can speak of "colloids" only as we speak of "crystals," "amorphous" substances, "soluble and insoluble" substances, or better still of "gaseous, liquid, and solid" substances. *All substances can appear as colloids under appropriate conditions.* This peculiarity of colloid-chemistry, through which it thus presents itself not as a study of colloid substances but as a study of the *colloid state*, will be discussed in detail later. But it is of great importance for even an elementary characterization of colloid substances to know that depending upon experimental conditions one and the same chemical compound can appear either as a colloid or as a non-colloid.

Generally speaking, the knowledge of the chemical constitution of a substance furnishes no trustworthy indication as to whether or not we are dealing with a colloid. Only one law has thus far been deduced governing the relation between chemical constitution and colloid state: *The more complex chemically the compound, the greater the probability that it is in a colloid state.* Thus most of the native proteins appear in a colloid state; and the chemical composition of the original colloid, namely gelatine, is so complex that we are still largely ignorant concerning it.

---

[1] See, for example, Koll.-Zeitschr., **2**, 53 (1907).

Solid and liquid and even gaseous bodies may appear in the colloid state.[1] The liquid colloids are the most numerous and the most important, and thus far have been most studied. Whenever we deal with the class properties of the colloids we therefore usually refer to these.

I. ELEMENTARY GENERAL COLLOID ANALYSIS

3. Chemically Homogeneous and Heterogeneous Liquids.— If we wish to inquire into the possible colloid nature of a given liquid, it is well to decide first whether it is *chemically homogeneous* or *chemically heterogeneous*.

In an ideal case a chemically homogeneous liquid has the following properties: 1. It is susceptible of hylotropic change, that is, it can be evaporated or frozen without changing its composition at any time during the manipulation. 2. The hylotropic transformations take place within *narrow* limits of temperature and pressure; there is only *one* boiling temperature and *one* congelation temperature; we speak of melting and boiling *points*. Among further properties of an ideal liquid is to be mentioned the fact that the temperature coefficient of its molar surface energy equals 2.12.[2]

As is well known, there are a great many substances, organic liquids, more particularly, which fulfill these requirements in part only. They are the mixtures of *isomeric, metameric, and polymeric* substances; to which we may add the so-called *associated* liquids. Even though all these liquids show the same elementary analysis in every state of aggregation, yet they can be separated by fractional distillation, for example, into parts having different boiling points; or, notwithstanding the analytically identical composition of the liquid undergoing distillation and the distillate, it is noted that the former is not *completely* evaporated at any definite temperature. These facts are illustrated by the behavior of polymerized liquids such as styrol-metastyrol. Again, as in associated liquids, the molar surface energy is found to be less than the normal.

The following rule may be stated regarding the relation of these properties to the possibility of the appearance of a colloid state in liquids of constant composition: *The more a liquid approaches the ideal of chemical homogeneity, the less probable that it is in the colloid state.* Therefore, if from general physico-chemical examination we know a liquid *not* to be "normal" with regard to exactness of boiling point, molar surface energy, etc., it is possible that we are dealing with a "physical mixture," and therefore with a molecular or colloid solution.

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[1] See page 43.

[2] See the textbook of Wilh. Ostwald, Grundr. d. allgem. Chemie, 4 Aufl., 1919 for a discussion of the general concepts of physical chemistry employed here.

Colloid liquids showing the same analytical composition with every hylotropic transformation are by no means rare. Thus far these have been little studied from a colloid-chemical point of view. Details regarding the peculiarities of these so-called *isodispersoids,* more especially the *isocolloids,*[1] will be given later. Nearly all the colloid solutions investigated thus far belong to the class of the chemically heterogeneous liquids discussed below. Since the fundamental properties of colloid liquids depend, not upon chemical composition but upon physical conditions which are especially to be encountered in chemically heterogeneous liquids, we shall also discuss in the succeeding paragraphs the general data by means of which we recognize the colloid character of chemically homogeneous liquids.

4. True Solutions, Mechanical Suspensions and Colloid Solutions.—Chemically *heterogeneous* liquids can be separated by changes in temperature and pressure (distillation, freezing, etc.) into at least *two* components of different chemical composition. When we have thus determined in our unknown that we are dealing with a chemically heterogeneous liquid it may appear in any one of three states:

(*a*) The unknown may be an ordinary or "true" (molecular-disperse) solution of one or more substances.

(*b*) It may be a coarse "mechanical suspension" of one or more substances which form true solutions to a limited degree only, if at all.

(*c*) It may be a colloid solution.

5. The Properties of Mechanical Suspensions.—In a qualitative analysis for the determination of the "degree of dispersion"[2] in a heterogeneous liquid the *second* of the above possibilities can be disposed of most easily. Typical "mechanical suspensions" of substances but slightly soluble in liquids, as suspensions of quartz, kaolin, or oil in water, are *turbid* in transmitted light, and their individual particles can be recognized under the *microscope* (though sometimes only with high magnifications and special optical means).

---

[1] Examples of such liquid isocolloids are oils, petroleum, paraffin, styrol-metastyrol, liquid sulphur at temperatures above 170°, highly polymerized liquids, etc.

[2] See page 29 for a discussion of the concept "degree of dispersion;" the three classes of systems mentioned above are distinguished from each other by their different degrees of dispersion.

If no microscope is available, *filtration* is the next simplest method by which a suspension can be recognized. Ordinary filter paper holds back particles having a diameter greater than about 5μ; a hardened filter (Schleicher and Schüll, No. 602 *e.h.*), those about 2μ in diameter. Clay cylinders and the so-called Pukall filters which are frequently employed in bacteriology will even hold back particles about 0.4 to 0.2μ in diameter.[1] The size of the particles in question can therefore be roughly measured by the employment of such differently permeable filters. When applied to *emulsions*, that is, suspensions of droplets of one liquid in another filtration is successful only when the suspended droplets are not materially *deformed* during filtration. As the investigations of E. Hatschek on the filtration of emulsions show, this difficulty does not appear if the droplets are moderately viscous, as are the droplets of castor oil or olive oil; or when their surfaces are in a condition which gives the droplets themselves sufficient stiffness. Such stiffness may result from the formation of thin elastic membranes about the droplets, of the nature of the well-known saponin or peptone films,[2] or it may be due—and this seems most important—to the *small size* of the droplets with its accompanying increase in surface energy. As E. Hatschek has shown, it is often possible to separate emulsions into their components by means of appropriate filters.

6. The Instability of Mechanical Suspensions.—Another characteristic of coarse suspensions of solid and liquid particles is their *instability*, that is their tendency to separate "spontaneously," *i.e.*, by the action of gravity, into their components. If we can exclude the stabilizing effects of additions of viscous substances such as gelatine, tragacanth, etc., as well as the peculiar

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[1] For details regarding permeability and size of pores in various filters see H. Bechhold, Zeitschr. f. physik. Chem., **64**, 342 (1908).

[2] E. Hatschek, Koll.-Zeitschr., **6**, 254 (1910); **7**, 81 (1910).

"protective action" of small amounts of soap, saponin, albumose, etc., separation occurs in typical coarse suspensions in accordance with the difference in the densities of their components.[1] Considerable acceleration in separation can be effected by moderately centrifuging the mixture. A hand-centrifuge such as is employed in the study of blood does very well. The suspended component then separates out, in accordance with the difference in density, either in the form of a *precipitate* or of a *supernatant layer*. After such a separation has been accomplished either by gravity or with the assistance of a centrifuge, the original system can in most instances be restored by *shaking* the components together again.

When the suspended particles are in a *very finely* divided condition, indefinite or negative results are obtained by these procedures. Under such circumstances two possibilities still remain: the liquid in question is either a "true" or a "colloid" solution.

7. Differentiation of a True from a Colloid Solution.—It is generally harder to distinguish a true from a colloid solution than to distinguish a coarse suspension from either, yet this problem is precisely the one that arises most frequently. We must therefore discuss the methods involved in detail.

A. *Optical Differences.*—Absolutely *clear* liquids are formed as a rule by substances in molecular or true solution. If a liquid (*which is not chemically homogeneous, and which is not a coarse suspension*) is seen to be *turbid*, we may suspect that it is a colloid solution. The existence of a slight turbidity may be recognized on inspection of a rather thick layer of the liquid in a thin-walled glass vessel against a dead black background (black paper, or better, black velvet). If the liquid is colorless but turbid, the background shining through it assumes a *grayish-white* appearance. In the case of colored liquids (in the examination of which it may be necessary to employ a particular dilution or thickness of layer) an optical effect appears which is similar to that observed on mixing water-colors with small quantities of opaque white (the colors become milky). Different varieties of nephelometers have been constructed for the more exact determination of the degree of turbidity.[1]

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[1] In this experiment it is well to use very long tubes and relatively "dilute" systems. The temperature must be kept constant to prevent mixing of the layers by convection currents. Closed basement rooms may be used if a suitable thermostat is not available.

8. The Tyndall Phenomenon.—A far more delicate method of demonstrating the presence of a very fine turbidity consists in the use of the so-called *Tyndall phenomenon*. It is well known that when, for example, the air of a room is intensely illuminated, say by sunlight, from one side only, dust particles are rendered visible which cannot be seen when illumination is equal on all sides. This is the prototype of the so-called Tyndall phenomenon, the theory of which will be discussed later. Extraordinarily fine turbidities can be rendered visible by such means; in fact this holds true to such an extent that special measures become necessary if we would obtain, for example, an absolutely "optically empty" distilled water; ordinary distilled water regularly shows individual dust particles.

FIG. 1.—*Tyndall* phenomenon.

Tyndall experiments can be best carried out where sunlight and a darkened room are available. The phenomenon becomes beautifully evident if we but let a sharply defined ray of light, entering a darkened room through a hole bored in the shutter of a window, pass through the liquid in question contained in a thin-walled test tube. Very good results are also obtained if a projection lantern is used from which the light rays are concentrated as much as possible by means of a condenser and diaphragm (see Fig. 1). A powerful incandescent lamp[1] enclosed in a box that is impervious to light and provided with a small opening, and if possible with a condenser, is generally satisfactory also. The thinnest and clearest glass vessels must be used. Special advantages are offered by vessels with parallel walls which reflect light least. When we work with hot or very cold liquids we use cotton-stoppered, double-walled tubes from which the air has been exhausted (Dewar tubes). When cold liquids are used in these, the tubes may be immersed in alcohol to avoid the condensation of water on their outer walls.

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[1] For simpler forms of such apparatus see H. von Oettingen, Zeitschr. f. physik. Chem., **33**, 1 (1900); J. Friedländer, ibid., **38**, 430 (1901).

It should now be noted that it is *not* the presence of many more or less evident particles which may be recognized either macroscopically or microscopically that distinguishes a colloid from a molecular-disperse (true) solution. It is rather the *intensity* of the unbroken light-cone passing through the solution which betrays the state of liquid. It is safe to say that *liquids which show no definite Tyndall light-cone or show it only in high concentrations are molecular-disperse solutions.* Practically all colloid solutions give a positive Tyndall effect.

The Tyndall phenomenon is not to be confounded with *fluorescence.* When a ray of light enters certain solutions, such as those of some dye-stuffs and alkaloids, the path of the beam betrays itself in brilliant colors even though these solutions may not be in the colloid state. The fluorescence can be distinguished from the Tyndall effect by looking at the light-cone with a Nicol prism. If we look at the Tyndall cone of a colloid solution through a Nicol prism we find that *it disappears when the prism is rotated, to light up again at a certain angle.* Fluorescent light remains visible at all angles.

Emphasis should be laid on the fact that the Tyndall effect is of particular value in the recognition of *isocolloids.*

It should further be mentioned that the microscopic examination of a Tyndall cone with the highest available magnifications at times permits us to see the individual particles which in their totality give rise to the light-cone. This is called *ultramicroscopy*. Since for ultramicroscopy special apparatus and powerful sources of light are necessary which are by no means generally available, and since the technique of ultramicroscopy is by no means simple, we cannot further discuss the subject in this elementary outline of colloid analysis.

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[1] Not only electrically lighted but gas-lighted projection apparatus as used in photographic enlarging, when combined with a condenser is suited for this purpose.

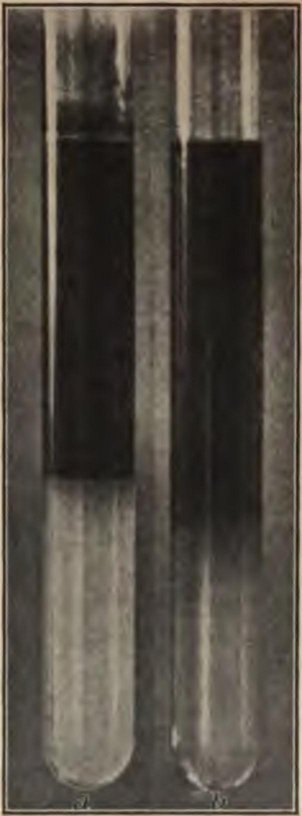


FIG. 2.—Diffusion experiments with gelatine gels at end of 24 hours. (*a*) (colloid) congo red; (*b*) (molecularly dispersed) safranin.

9. The Distinction of True from Colloid Solutions on the Basis of Their Mechanical Properties.—

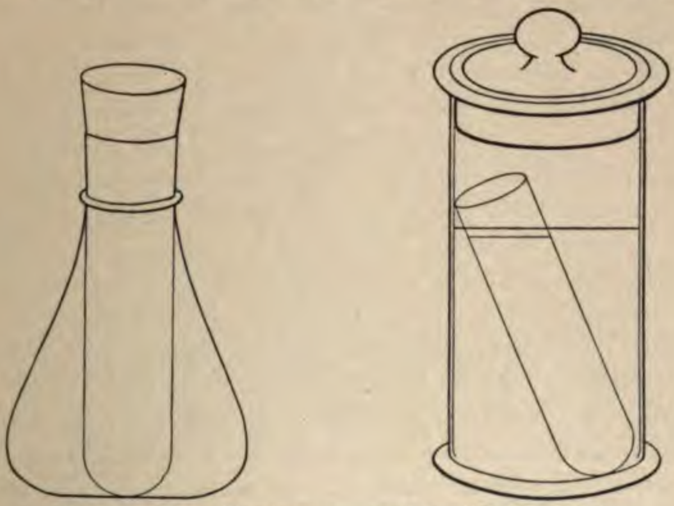
B. *Mechanical Differences.—Diffusion* and *dialysis* experiments provide us with two further simple methods for distinguishing molecular-disperse (true) from colloid solutions. These might be called the "classical" methods for the qualitative analysis of solutions, for it was by them that Thomas Graham in 1861 first distinguished between the "states" of different solutions and thus introduced the concept "colloid."

(*a*) *Diffusion Experiments.* — Perhaps the simplest and most convenient experimental method of estimating the *diffusion velocity* of a dissolved substance depends upon the fact that moderately concentrated jellies of gelatine, agar, etc., offer only slight or no resistance to the diffusion of substances through them, as determined by comparison with the diffusion of these same substances through the pure solvent. For such tests we prepare a 5 percent gelatine, or better a 2 percent agar solution, fill some test tubes about halfway with the hot solution, and allow it to congeal. It is well to use gelatinizing substances that have been thoroughly washed and *purified*. The solution under examination is then poured upon these gelatine or agar layers and the tubes are left standing, variations in temperature being avoided as far as possible. A true solution in water, either of a dye such as safranin, or of a colored salt such as copper sulphate is taken as a control. If the solution undergoing analysis is colored a picture similar to that shown in Fig. 2 may be seen after a day or two. While non-colloids, that is molecular-disperse or true solutions, gradually spread down into the jelly, colloid solutions do this only very slightly or not at all. *In other words, substances in the colloid state practically do not diffuse at all. At the best they diffuse with extreme slowness when compared with the behavior of substances in molecular solution.*

If it is feared that a liquid of high specific gravity may by mechanical means force itself into the jelly, a small tube half filled with gelatine or agar may be placed mouth downward into the solution contained in a second larger vessel. The tube is removed after a few days and carefully washed when it also will show the phenomena that have been described. If the liquid under examination is light colored or *colorless* the test tube containing the gelatine or agar is dipped for an instant into hot water so that the jelly slips out. This is then divided into several slices of equal size, and the individual slices are examined analytically for their content of the substance in question.

This method is not generally applicable to the analysis of *isocolloids*, nor when marked chemical or colloid-chemical reactions take place between the jelly and the liquid under examination. Under such circumstances it is necessary to resort to other methods.

10. Dialysis Experiments.—(*b*) *Dialysis*, a process closely related to diffusion, depends upon the fact that many animal, vegetable and artificial membranes hold back substances in colloid solution while they allow substances in molecular solution to pass through them whenever such a membrane separates the liquid under examination from the pure dispersion medium (the solvent). Parchment bags, so-called diffusion thimbles made in one piece (see Figs. 3 and 4), pig and fish bladders, and artificially prepared colloid membranes form the most convenient as well as the most frequently employed of these. The last-named are made by dipping a large, well-cleaned test tube into collodion dissolved in ether and alcohol, permitting the collodion layer formed to harden slightly by evaporation, repeating the process if necessary, and then hardening the whole by washing in water. The collodion bag is then carefully drawn off the tube.[1] When only small amounts of liquid are to be analyzed colloidally, diffusion thimbles (Schleicher and Schüll) arranged as shown in Fig. 3 are particularly useful. For this purpose a small Erlenmeyer flask is used, into the neck of which the diffusion thimble fits snugly; the flask is first filled with pure solvent while the liquid under examination is poured into the thimble which is then closed with a cork stopper. In this way, aided by the slight swelling of the thimble which usually occurs, evaporation and the entrance of dust into the liquid are largely prevented. It is evident that if the solutions under examination are alcoholic or ethereal in character, collodion thimbles cannot be used. When dealing with such volatile liquids it is advisable to employ glass-stoppered vessels in which the dialyzer is placed or suspended as shown in Fig. 4. *The dialyzer distinguishes colloid from crystalloid solutions in that it does not allow the former to pass through the membrane into the outer liquid.* Occasionally we find that a colloid "phase" will pass



FIGS. 3 and 4.—Simple arrangement for dialytic analysis.

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[1] Details of various methods of preparation may be found in A. Cotton and H. Mouton: Les Ultramicroscopes, 117, Paris, 1906; L. Bigelow, Journ. Am. Chem. Soc., **29,** 1576 (1907); J. Duclaux, Journ. Chem. Phys., **7,** 430 (1909); W. Biltz and A. von Vegesack, Zeitschr. f. physik. Chem., **63,** 369 (1909).

together with a molecularly dissolved phase into the outer liquid. But this happens only at first. After the outer liquid has been renewed once or twice, no more of the colloid phase comes through. Sometimes a dissolved substance will penetrate a collodion membrane when it is held back by the less porous parchment paper. In such cases we are evidently dealing with a "highly disperse" (finely divided) colloid, or to put it in another way, with a substance occupying a position midway between the colloid and molecular-disperse state.

So-called ultrafilters are used for more exact determinations of the degree of subdivision, but they cannot be discussed here because they are rather complex (see later).

11. **Transition Systems.**—It will nearly always be possible to determine by one or more of the methods described whether a substance in solution is in the colloid or in the molecular-disperse state. At the same time it must be admitted that we encounter cases in which one and the same liquid yields different results with different methods. Thus a pure congo red shows only a faint Tyndall cone, yet it scarcely diffuses through parchment paper. Protein solutions behave in a similar way in certain concentrations, etc. For a complete analysis it is therefore not only advisable but necessary to employ several methods. But even then it may occasionally be doubtful whether we are dealing with a colloid or with a molecular-disperse solution. These cases constitute the extremely interesting *transitional types* between the two kinds of solution. Their state can be completely analyzed only by application to them of the more refined methods of colloid and physical chemistry—ultramicroscopy, ultrafiltration, molecular weight determination, etc.

II. ELEMENTARY SPECIAL COLLOID ANALYSIS

12. **Suspensoids and Emulsoids.**—When one undertakes detailed work with substances in the colloid state one soon discovers that the individual illustrations arrange themselves in two classes of systems which differ markedly from each other, in spite of the fact that all are possessed of the same general properties that we have already discussed. These two groups of colloid solutions are the *suspension colloids* (suspensoids) and

the *emulsion colloids* (emulsoids), or as they are also called, the *lyophobic* (hydrophobic) and *lyophilic* (hydrophilic) colloids. The theoretical basis for such nomenclature will be discussed later. In passing, it should be noted that the two terminologies are not entirely synonymous, though for practical purposes they may be so regarded. When by the general methods previously discussed we have discovered that we are dealing with a colloid solution we have next to determine whether it is a suspensoid or an emulsoid. Of the many means of doing this we describe the following because they are particularly characteristic and simplest in character.

13. **Viscosity.**—The viscosity of a suspension colloid, particularly in low concentration, is imperceptibly greater than that of the pure dispersion medium (the pure solvent). In contradistinction, the viscosity of an emulsion colloid even in low concentration is much greater than that of its dispersion medium; in fact at higher concentrations this becomes so great that the colloid solution assumes an oily or even a gelatinous consistency. Further, the viscosity of an emulsion colloid generally increases rapidly with decrease in temperature which is not the case with a suspension colloid. The simplest way of estimating experimentally the viscosity of a colloid solution and its variations with temperature and concentration is to measure the time of outflow of a constant volume of liquid from a standard volumetric (10 cç.) pipette. Roughly, the viscosity is inversely proportional to the time of outflow.

14. **Coagulation.**—It is characteristic of colloid solutions that the substance in colloid solution may be easily precipitated or "coagulated" through various agencies (see Figs. 5 and 6). Electrolytes such as neutral salts are particularly effective. *The suspension colloids are easily coagulated when minute quantities of salts, especially those having a polyvalent ion, are added to them, while the emulsion colloids are precipitated only after the addition of much larger quantities of salt.* This is particularly true of hydrosols, that is of colloids having water as the dispersion medium. If, for example, aluminium sulphate (ordinary alum serves the same purpose) is selected as the coagulant, it is found that almost all suspension colloids are precipitated by this as soon as it is present in a 1 percent concentration. Much higher

concentrations are necessary to precipitate the typical emulsion colloids. In fact the coagulation of many emulsion colloids is not brought about until the neutral salts have been added to the point of saturation. In making these qualitative analyses one must not use *salts of the heavy metals,* for they frequently produce entirely abnormal coagulation effects.

15. Influence of Concentration.—One will occasionally encounter instances in which neither viscosity nor coagulation determinations will serve to distinguish clearly a suspension colloid from an emulsion colloid. It is then advisable to compare with each other rather dilute solutions of suspension colloids and rather concentrated solutions of emulsion colloids. We encounter here also a series of interesting transitional types which can be accurately analyzed only through quantitative study. The suspensoid or emulsoid state is not a constant or integral property of a chemical *substance,* it is the result of a series of physico-chemical variables which bring about a particular *state* in a chemical substance.

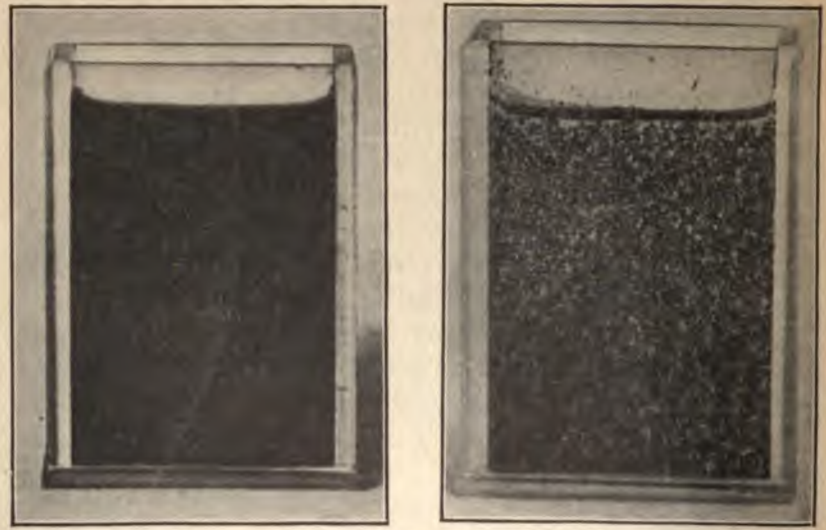

FIG. 5.—Non-coagulated. FIG. 6.—Coagulated through addition of 2 percent sulphuric acid.

Coagulation of an aqueous suspension of lamp-black. (After *E. E. Free.*)

16. The Electric Properties of Colloids.—Colloid solutions have a characteristic electric behavior which explains many of their peculiar properties. Most substances in colloid solution assume an electric charge toward their dispersion medium, though the magnitude of this charge varies greatly. We are able to distinguish between negatively and positively charged substances in colloid solutions. The simplest method of determining with which of these we are dealing in a given case is to make use of their difference in behavior (as noted by F. Fichter and N. Sahlbohm) when they are subjected to *capillary analysis* by means of filter paper. If the lower end of a strip of filter paper is immersed in a colloid solution one of two things may happen depending upon the sign of the electric charge of the colloid; if the colloid carries a negative charge it wanders up the strip of paper along with its dispersion medium. The colloid may rise to a height of 20 centimeters or more depending upon the kind of paper used and the special properties of the colloid. If the

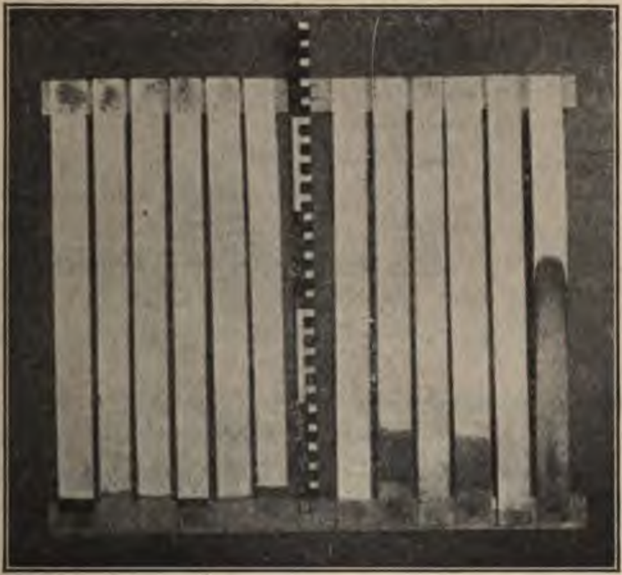

FIG. 7.—Ascent of positively and negatively charged colloids. (According to *N. Sahlbohm.*)

The dispersion medium ascends the paper in *all* these experiments, but as shown in the left half of the photograph, the positively charged colloids (metallic oxides) are precipitated at once at the margin of immersion. The negatively charged colloids, on the other hand, (gold, silver, arsenious sulphide, antimony sulphide, Berlin blue, selenium) ascend with the dispersion medium, being separated from its upper margin by a diffusely stained area.

colloid carries a positive charge the dispersion medium continues to rise to the normal height, but the *colloid phase does not.* It rises to a point but slightly above the level of the liquid in which the filter paper is immersed, becomes highly concentrated here and finally coagulates. Positively charged colloids may therefore be separated from their dispersion medium through the capillary action of strips of filter paper. The behavior is illustrated in the accompanying Fig. 7, taken from N. Sahlbohm.

17. The Mutual Precipitation of Colloids.—Another means of determining quickly the sign of the charge of a substance in colloid solution depends upon the fact that *oppositely charged colloids precipitate each other.* If two typical test solutions are kept in stock (for example, a positive colloid such as ferric hydroxide, and a negative colloid such as sulphur or arsenious sulphide) the charge of an unknown colloid may frequently be determined by ascertaining with which of the two solutions it yields a precipitate. The charge of the unknown colloid is then the opposite of that of the precipitating colloid the charge of which is known. This method is not, however, universally applicable.

18. Electrophoresis.—The sign of the charge of the colloid phase may be determined by noting the direction in which it moves when subjected to the action of an electric current (migration in an electric field). To do this the colloid is poured into a U tube closed with corks and provided with platinum electrodes which dip into the solution. When a stronger current is not available, that from a few storage cells will frequently suffice to produce a movement of the colloid toward one or the other pole if only sufficient time be allowed. If the colloid wanders toward the anode it is negatively charged; if it wanders toward the cathode it is positively charged. Disturbing secondary effects often enter into the behavior of a colloid when subjected to the electric current, and so it is advisable to employ along with it the methods of colloid analysis already described.

If the colloid under examination is colorless it may be necessary to call in the aid of simple analytical methods.

19. Summary.—The following is an outline of the methods of qualitative colloid-chemical analysis discussed above.

A. ELEMENTARY GENERAL COLLOID ANALYSIS

I. *Chemically Homogeneous Liquids.*

(*a*) Always hylotropically transformable, definite boiling and freezing points, normal molecular surface energy, etc.	Normal liquids.
(*b*) Physical mixtures of substances having the same chemical composition, but different "body properties" as different boiling points, molecular surface energies, etc.; mixtures of isomeric and polymeric substances, highly associated liquids, etc.	Isodispersoids, possibly Isocolloids.[1]

II. *Chemically Heterogeneous Liquids.*

(*c*) Microscopically heterogeneous, components separable by ordinary filtration, may be easily sedimented especially if centrifuged, settle spontaneously, can usually be easily resuspended on shaking.	Coarse dispersions (suspensions and emulsions).
(*d*) Optically homogeneous, at least in low concentrations, diffuse well (as into gelatine or agar-agar), and pass through membranes (as when subjected to dialysis), etc.	Molecular-disperse solutions.
(*e*) Often turbid macroscopically, Tyndall test positive (apply Nicol prism to differentiate from fluorescence), non-diffusible or only slightly so, will not pass through a membrane, etc.	Colloid solutions.

B. ELEMENTARY SPECIAL COLLOID ANALYSIS

(*f*) Viscosity not perceptibly greater than that of dispersion medium; easily coagulable by electrolytes, especially by salts with polyvalent ions (1 percent alum).	Suspension colloids (lyophobic colloids).
(*g*) Viscosity substantially greater than that of pure dispersion medium even in low concentrations. Viscosity increases with lowering of temperature; difficultly coagulable by salts which at times need to be added to saturation point to accomplish flocculation.	Emulsion colloids (lyophilic colloids).
(*h*) Electric behavior:	
1. Colloids can be separated from their dispersion medium by capillary analysis (filter-paper experiment); are precipitated on adding colloid solutions of sulphur or arsenious sulphide; wander toward cathode.	Positive colloids.
2. Can be separated but slightly, if at all, from their dispersion medium (filter-paper experiment); are precipitated by colloid hydroxide solutions; wander toward anode.	Negative colloids.

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[1] For details see §18, page 102.

PART I

GENERAL COLLOID-CHEMISTRY

(THEORY OF THE COLLOID STATE)

CHAPTER I

THE GENERAL CONSTITUTION OF COLLOID SYSTEMS

§2. The Colloids as Heterogeneous Systems

1. The Concept of Heterogeneity.—The typical colloids, more particularly the colloid solutions, belong to the group of systems designated as *polyphasic* or *heterogeneous* by physical chemists. This is the broadest as well as the best established generalization thus far derived from the study of colloid-chemistry.

By a phase is meant any homogeneous part of a system different from other parts of the system and separated from these by *abrupt* transitions. Thus we distinguish a gaseous and a liquid phase in a closed vessel which is half filled with water; we obtain two liquid phases when we mix water with carbon disulphide; we get a solid and a liquid phase when we shake up quartz dust in water. Sudden changes, more particularly in physical properties, are encountered as a rule as we pass from one phase to another in these systems, or, to put it more simply, we recognize that there exist *boundaries* or *surfaces* between them. These changes may be due either to the fact that the different phases possess totally different properties, or there may be simply a quantitative difference in the properties possessed by each. We may therefore speak of different *kinds* and of different degrees of heterogeneity. Thus two phases may be heterogeneous optically but homogeneous electrically or thermally. It has further been found that, as a rule, more of the physical and physico-chemical properties of the different constituents of a system change at the surfaces of contact when a solid phase and a liquid phase coexist than when two (non-miscible) liquid phases coexist. Failure to state the exact properties referred to in arguing for the heterogeneity of colloid systems has undoubtedly been the cause of much misunderstanding in the discussion of this question. It must also be remembered that the general constitution of boundary surfaces must tend to vary the more, the greater the differences in the nature and the larger the number of the properties which change abruptly at them. In this sense the suface where a liquid comes in contact with another liquid may be said to be less well defined than that where a liquid comes in contact with a solid. The importance of making such a distinction has repeatedly shown itself in the literature of colloid-chemistry as we shall see later.

2. **Physical and Chemical Heterogeneity.**—The relation between *chemical* (analytical) and *physical* heterogeneity is of especial importance for the exact characterization of the colloids as heterogeneous systems. It has been found that *two spatially different parts of a system having the same chemical composition (chemically homogeneous therefore), may physically show typical boundaries between them*, in other words appear as different phases. In illustration of this fact we need but call to mind the *allotropic* modifications of the elements which may coexist for a long time, as in the case of sulphur. But *compounds* of the same composition, particularly isomers and polymers, may also form heterogeneous systems. Thus the solid particles of metastyrol may be suspended in liquid styrol; rubber may be "dissolved" in isoprene, etc. It is even possible to have coexist hylotropic phases (different states) of one and the same chemical substance, though usually but temporarily. Thus water and steam, or water and ice may coexist.

It follows from all this that the spatial or other heterogeneity of the colloids is not necessarily connected with a *chemical* heterogeneity if by the latter is meant a difference in analytical composition. The existence of *physical* boundary surfaces in them can alone be regarded as characteristic of them. As a matter of fact we can distinguish between the different phases having the same chemical composition in the illustrations instanced above not only by differences in their chemical reactivity, but by optical differences, by differences in states of aggregation, etc., in other words by their different "body properties."

But whenever we speak of (physically) heterogeneous systems we mean spatial combinations of coexisting phases. There are several types of these. Thus we have systems in which all the phases are liquid, others in which they are all solid, still others in which solid, liquid and gaseous phases are mixed. Heterogeneous systems composed of gases only cannot long exist, for gases are miscible with each other in all proportions (see p. 43).

§3. Colloids as Disperse Heterogeneous Systems

Ordinarily the number of phases and their state of aggregation in a heterogeneous system can be determined by mere macroscopic examination. We need but to call to mind the above-mentioned examples of heterogeneous systems. The following two peculiarities serve to distinguish the colloid solutions from these *macroheterogeneous* systems.

1. The Phases are in Contact with Each Other under Conditions which Permit the Development of much Surface between Them.—First, the amount of the *absolute* surface with which the various phases are in contact with each other is very great. Second, and more important and characteristic is the fact that the magnitude of the *specific surface*,[1] that is the quotient of the surface divided by the volume is extraordinarily great in colloid systems. This property may also be expressed by saying that there is a great concentration of surface in the unit volume. At first sight one might believe that the *small size* of the individual particles characterizes this class of heterogeneous systems. In fact we frequently speak of the great *dispersion* or *subdivision* of the phases. Nevertheless, it should be noted that it is only because a *great number* of such small particles exist in a relatively small volume that the peculiarities of such systems are produced. From this it should also be clear that it is not the absolute amount of surface which is of such importance as the relative or specific surface.

2. The Phases are so Distributed within the System that Externally the Whole Appears Homogeneous.—Unless an exceedingly small amount is studied, every fraction of a colloid solution has the same average composition. This second peculiarity is evidently closely connected with that given above, for a spatially uniform distribution of the phases is made possible only through the existence of a great specific surface. To express it in more exact terms, the uniformity of this distribution in a given volume increases with the degree of subdivision of the phases.

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[1] Wo. Ostwald, Pflüger's Arch. f. d. ges. Physiol., **94**, 251 (1903). See also J. M. van Bemmelen, Die Absorption, Ges. Abhandl., 23, Dresden, 1910.

It should be emphasized that the first-mentioned property is more important and more characteristic of these bodies than the uniform distribution of the phases in space. It must be admitted that the conception of "colloid" or, more correctly speaking, of "colloid state" was developed in connection with the study of bodies belonging to the spatially homogeneous systems, that is to say, in connection with the study of colloid solutions. But there are systems which also belong to the field of colloid-chemistry in which the phases are *not* uniformly distributed within each other. To the former systems belong, for example, bodies which are in the course of swelling or bodies which have attained their maximum of swellling in the presence of an excess of the solution in which they are swelling. On the other hand, colloid solutions in the process of coagulating are systems which are losing their condition of spatial homogeneity. It is evident that processes of swelling tend toward the production of a spatially homogeneous system in the sense in which this term was used above. On the other hand, the process of coagulation arises in a homogeneous system. It is because these bodies have in their past been in, or tend in their future to assume, a spatially homogeneous condition that they belong to the class of systems here under discussion.

It follows from these considerations that the *colloid solutions* occupy an intermediate position in colloid-chemistry, and that they should always be meant when colloids in general are under discussion. Thomas Graham introduced the useful special name of *sol* for these spatially homogeneous systems. In contradistinction, systems in the course of passing to or from a condition of spatial homogeneity he calls *gels*.

Heterogeneous systems with the two peculiarities mentioned are known as *disperse* heterogeneous systems, as suggested by Wolfgang Ostwald[1] or simply as "*dispersoids*," an abbreviation proposed by P. P. von Weimarn.[2] The term "*microheterogeneous*" systems, put forward by G. Bredig,[3] is synonymous with these. The broadest generalization resulting from the investigation of the colloids seems therefore to be the establishment of the fact that they are a part of the general class of the dispersoids, in other words the colloid state of a substance is a special case of the dispersoid state.

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[1] Wo. Ostwald, Koll.-Zeitschr., **1**, 291, 331 (1907).

[2] P. P. von Weimarn, Koll.-Zeitschr., **3**, 26 (1908). von Weimarn uses this term in a somewhat modified sense.

[3] G. Bredig, Zeitschr. f. Elektrochem., **12**, 589 (1906).

§4. The Disperse Phase and the Dispersion Medium

Detailed examination of a simple dispersoid, a suspension let us say, at once lets us recognize the fact that the two phases are *geometrically* or *as regards their shape* different from each other. Most frequently one phase is composed of a great number of individual particles which are *separated* from each other. Because these particles have for the most part the same properties, we are accustomed to consider them as a whole and so to designate them as *one* phase. The individual particles of such a phase may approximate the spherical in form, but they may also be crystalline; further, they may be mobile or immobile. The second phase is usually *continuous* and lies between the particles, droplets or bubbles of the first phase. The first phase is therefore generally suspended in the second. As we must frequently distinguish between the two phases they have received special names. The finely subdivided discontinuous phase is called the *disperse phase;* the other, continuous or "closed" phase is known as the *dispersion medium.*[1] English writers are in the habit of calling the disperse phase the "internal phase," the dispersion medium the "external phase." French investigators distinguish between the "micelles, granules colloidaux" and the "milieu extérieur."

This normal geometrical constitution may in some instances give place to a more complex one depending particularly upon the behavior of the disperse phase. The disperse phase may also be continuous and may then extend through the dispersion medium in the form of a sponge or network. Such systems are formed in the first stages of many processes of coagulation. Evidently when the disperse phase and the dispersion medium bear such a relationship to each other the geometrical distinction between them disappears; one can then at best only designate the phase present in excess as the dispersion medium.

Relations become more complex when heterogeneous systems with more than two phases are considered. In the more important and typical cases several disperse phases may exist in the form of spatially discrete particles in a common dispersion medium. All reactions between colloids, like those of the immune bodies, take place in a common dispersion medium. On the other hand, systems in which one of the disperse phases is continuous while another consists of individual particles are represented by membranes of colloid origin through which a colloid solution is being filtered.

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[1] Wo. Ostwald, Koll.-Zeitschr., 1, 291, 331 (1907).

§5. Specific Surface in Dispersoids; Degree of Dispersion

It has been stated that the chief characteristic of the dispersoids is the great development of surface by their phases or the high value of their specific surface. It should now be noted that the following three kinds of specific surface may be distinguished in a typical diphasic dispersoid:

1. $$\frac{\text{The absolute surface of the entire disperse phase}}{\text{The total volume of the disperse phase}}$$

2. $$\frac{\text{The absolute surface of the dispersion medium}}{\text{The total volume of the dispersion medium}}$$

3. $$\frac{\text{The absolute surface of an \textit{individual} particle of the disperse phase}}{\text{The volume of an \textit{individual} particle of the disperse phase}}$$

The first-named specific surface is undoubtedly the most characteristic of such a system. All three specific surfaces may, but two of them must, change in value whenever changes occur in a dispersoid, which are accompanied by changes of surface. Thus if a suspension of quartz particles is diluted, only the two first-named specific surfaces change in value. In *colloid* systems, however, the third specific surface or the size of the disperse particles often also varies with the changes in concentration, as will be shown later. As a rule all three specific surfaces are diminished in processes of coagulation.

Let us now turn to a specific illustration of how great are the values of the absolute and the specific surfaces in a dispersoid, and how quickly these values increase with the progressive subdivision of one of the phases. If we assume that the given volume undergoing subdivision has and maintains cubical form then Table 1 illustrates the increase in the total and specific volumes if the division takes place decimally.

TABLE 1.—INCREASE IN THE SURFACE OF A CUBE WITH PROGRESSIVE DECIMAL SUBDIVISION

Length of one edge	Number of cubes	Total surface	Specific surface
1 cm.	1	6 square cm.	6
1 mm. = 1×10^{-1} cm.	10^3	60 square cm.	6.10^1
0.1 mm. = 1×10^{-2} cm.	10^6	600 square cm.	6.10^2
0.01 mm. = 1×10^{-3} cm.	10^9	6000 square cm.	6.10^3
1.0 μ = 1×10^{-4} cm.	10^{12}	6 square m.	6.10^4
0.1 μ = 1×10^{-5} cm.	10^{15}	60 square m.	6.10^5
0.01 μ = 1×10^{-6} cm.	10^{18}	600 square m.	6.10^6
1.0 $\mu\mu$ = 1×10^{-7} cm.	10^{21}	6000 square cm.	6.10^7
0.1 $\mu\mu$ = 1×10^{-8} cm.	10^{24}	6 hectares	6.10^8
0.01 $\mu\mu$ = 1×10^{-9} cm.	10^{27}	60 hectares	6.10^9
0.001 $\mu\mu$ = 1×10^{-10} cm.	10^{30}	6 square km.	6.10^{10}

Particles somewhat less than 10$\mu\mu$ in diameter may be distinguished optically by means of the Ultramicroscope of H. Siedentopf and R. Zsigmondy. A 1 cm. cube of metallic gold subdivided up to the limit of ultramicroscopic visibility would therefore have a total surface of over 600 square meters and a specific surface of 6.10^6. Even at this point we begin to enter the sphere of molecular dimensions. Lobry de Bruyn and Wolff[1] for instance, calculated an approximate diameter of 5$\mu\mu$ for the starch molecule. If a cubic centimeter of dry starch could be subdivided into molecules, that is if it could be "dissolved" in the ordinary sense of the word, the starch would present a total surface of several thousand square meters toward the solvent. When we deal with the molecular dimensions of gases and of substances in crystalloid solution, assuming for their average molecular diameter the value of 1.10^{-8} we obtain values of several hectares for 1 cubic centimeter of dissolved substance. Thus in 100 cc. of a 10 percent sugar solution there would be an "internal surface" of about 50 hectares when the smallest possible surface, the surface of a sphere, is assigned to the sugar molecule. Finally, if it is assumed that ions and electrons are also separated through surfaces from their dispersion media (and an electrical heterogeneity and the existence of electrical surfaces must be postulated in these) the absolute and especially the specific surfaces attain enormous values.

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[1] Lobry de Bruyn and Wolff, Rec. Trav. chim. Pays, Bas., **23**, 155 (1904).

It should further be noted that the increase in the surface of a cube with progressive subdivision may be expressed by the formula:

$$\Sigma O = 6\left(\frac{a}{m}\right)^2 \cdot m^3 = 6a^2m$$

in which ΣO is the total surface in square centimeters, a, the length of one edge in centimeters, and m^3, the number of cubes. The original volume was taken as equal to 1 cc. (H. Mayer).[1] Since the unit of *specific* surface $= \frac{1\text{cm}^2}{1\text{cm}^3}$, then if a is taken as equal to 1, the calculated values obtained for surface represent at the same time the specific surface or the degree of dispersion.[2]

The concept of specific surface may conveniently be replaced by the somewhat clearer one of "*degree of dispersion*." Thus we may say that the degree of dispersion increases greatly with progressive subdivision of a given phase, etc.

As is well known, the surfaces of solid and liquid bodies of even ordinary dimensions already exhibit a whole series of peculiar phenomena, the intensity of which increases in direct proportion with the absolute and specific surfaces of the bodies. As examples might be mentioned the condensation of gases on solid surfaces, the manifold effects of surface tension in liquids, the fact that the majority of electrical phenomena appear at surfaces, etc. It should be remembered, however, that in such behavior the absolute surface is less responsible for these phenomena than the specific surface. Thus a few milligrams of platinum black have an effect upon an explosive gas mixture which is not equaled by that of several square meters of sheet platinum, for while they may have approximately equal *absolute* surfaces the former has an enormously greater *specific* surface. We are driven to conclude that all the phenomena observable at ordinary surfaces increase enormously in intensity and that they may even change qualitatively when we come to deal with dispersoids with their immense internal surfaces. There are also certain forms of energy that play an insignificant rôle in macroheterogeneous systems, but an enormous one in dispersoids.

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[1] H. Mayer, Kolloidchem. Beihefte, 1, 62 (1909).

[2] See also Wilh. Ostwald, Grundr. d. allg. Chemie, 4 Aufl. 531, Leipzig, 1909.

§6. Classification of the Dispersoids According to Their Degree of Dispersion

1. Classification of Zsigmondy.—It is evident that either the degree of dispersion or the number of phases in a system may be used for classifying the dispersoids. The mere number of phases is relatively unimportant as a means of classification, for the majority of the dispersoids and of the colloids in particular are either diphasic or triphasic. Classification on the basis of the degree of subdivision permits finer distinctions.

R. Zsigmondy[1] has developed a classification on this basis. According to him the field of colloid-chemistry occupies a middle position among the dispersoids thus far known. Particles about 0.1μ in diameter, that is, particles with a specific surface of about 6.10^5 (see Fig. 8), are stated by R. Zsigmondy to represent the *lower* limit of dispersion. The size of such particles is about that of the particles in emulsions and suspensions which no longer undergo separation. The value 0.1μ about represents the limit of microscopic visibility. According to Zsigmondy the field of colloid-chemistry begins with particles of this size and extends to particles about $1\mu\mu$ in size, that is, to such as have a specific surface or degree of dispersion of about 6.10^7, assuming that the particles are cubiform. The value $1\mu\mu$ is rather lower than the diameter of the smallest particles hitherto observed by ultramicroscopic means (about $6\mu\mu$). On this basis of classification the colloids represent dispersions of a magnitude varying between 6.10^5 and 6.10^7.

H. Siedentopf[2] and R. Zsigmondy[3] have proposed a nomenclature for the individual particles of typical dispersoids which is based upon their degree of dispersion. Particles visible under the microscope are termed "*microns*," while those which can be seen only by the application of ultramicroscopic methods are called "*submicrons*" or "*ultramicrons*." The disperse phase of colloid solutions would therefore be made up of submicrons (ultramicrons). It can be shown in several ways that particles exist whose size we know to be beyond that of ultramicroscopic visibility. They must therefore be less than $6\mu\mu$ in diameter.

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[1] R. Zsigmondy, Zur Erkenntnis der Kolloide, 22, Jena, 1905.
[2] H. Siedentopf, Berl. klin. Woch., Nr. 32, (1904).
[3] R. Zsigmondy, Zur Erkenntnis der Kolloide, 87, Jena, 1905.

These particles to which molecules and the products of their dissociation belong, are called "*amicrons.*"

The accompanying Fig. 8 (based chiefly on the data of R. Zsigmondy) is designed to illustrate approximately the relative sizes of the particles in typical dispersoids which have been the object of study. According to this diagram human blood corpuscles, starch granules, kaolin, and mastic particles would be *microns*, gold particles would be *submicrons*, while the finest gold

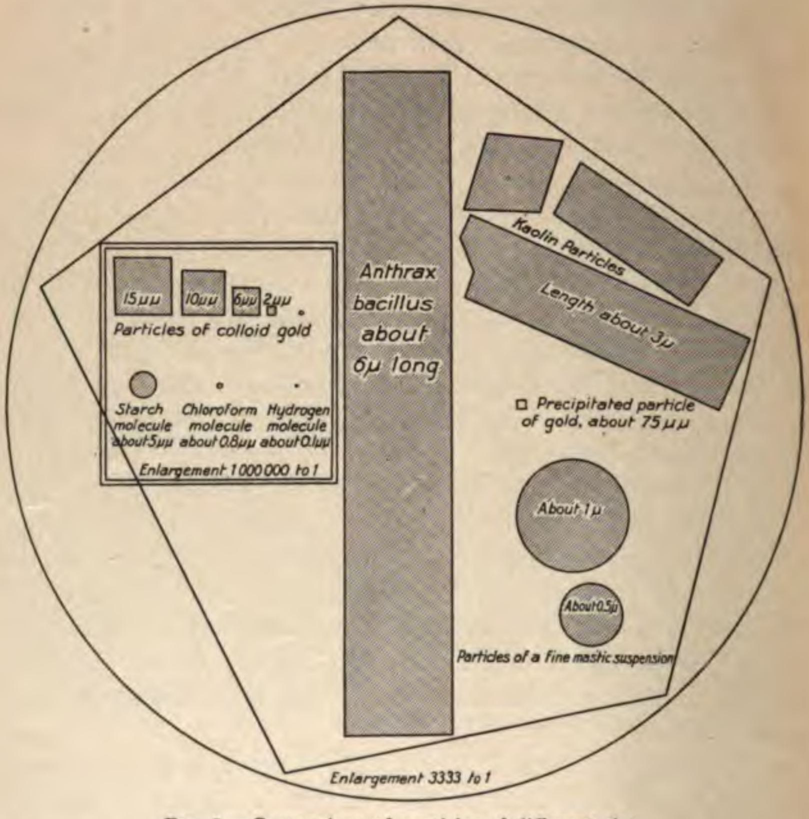
15μμ
10μμ
6μμ
2μμ
Particles of colloid gold
Starch molecule about 5μμ
Chloroform molecule about 0.8μμ
Hydrogen molecule about 0.1μμ
Enlargement 1000000 to 1
Anthrax bacillus about 6μ long
Kaolin Particles
Length about 3μ
Precipitated particle of gold, about 75μμ
About 1μ
About 0.5μ
Particles of a Fine mastic suspension
Enlargement 3333 to 1

FIG. 8.—Comparison of particles of different size.

The large circle corresponds to the diameter of a human red blood corpuscle (about 7.5 μ); the large pentagon to that of a starch granule of medium size (about 7.0 μ). The particles enclosed in the frame are, in comparison with the rest of the figure, enlarged 333 times.

The figure has been constructed from data and tables given in *R. Zsigmondy* (Zur Erkenntnis der Kolloide, Jena, 1905). The values for the mastic suspension are taken from *J. Perrin's* studies [Kolloidchem. Beihefte **1**, 221 (1910)].

particles, starch molecules, etc., which cannot be made out ultramicroscopically would be *amicrons*.

It seems of interest to give here the estimated diameters of a number of molecules. The smallest molecule seems to be that of hydrogen gas, 0.067 to $0.159\mu\mu$; water vapor has a molecular diameter approximating $0.113\mu\mu$; carbon dioxide one of about $0.285\mu\mu$,[1] etc. Different methods of calculation yield different values, yet all approach the magnitude $0.1\mu\mu$ or 1.10^{-8} cm. The molecular diameters of hydrated ions have recently been measured in several ways.[2] The molecular diameter of NaCl was found to be $0.26\mu\mu$; that of sugar, $0.7\mu\mu$, etc.

2. Classification of Dispersoids According to Their Degree of Dispersion.—It follows from Zsigmondy's classification that dispersoids having a very small or a very high degree of dispersion do not belong to the systems to be specially considered in this book. Such dispersoids should have special names. Dispersoids with a degree of dispersion of less than 6.10^5, that is microscopic suspensions, emulsions, and foams, might be called "*true or coarse dispersions*," while dispersoids with a degree of dispersion higher than 6.10^7 might be termed "*molecular dispersoids*." Roughly, the molecular dispersoids correspond with Thomas Graham's "crystalloids." As this term is based upon a property which does not necessarily determine the degree of dispersion it is not as free from objection as that which I suggest. Since molecules may dissociate into smaller particles, like ions, we obtain systems which may be designated as "ionically disperse" or as "*ionic dispersoids*," as suggested by The Svedberg.[3] It should be remembered, however, that ions are by no means always the products of dissociated molecules, and especially is this not true if such appear in colloid solutions. Such ions need not therefore have a higher degree of dispersion than the colloid particles themselves. This will be discussed later in the section on the electrochemistry of the colloids.

It has further been found that the specific surface of the colloids may vary within the limits calculated by Zsigmondy, that is to say, between 6.10^5 and 6.10^7. We may therefore expect to find that colloid solutions contain particles of different sizes. Experimental study has confirmed this expectation. Not only have different colloids very different degrees of dispersion, but one and the same substance may exist in different degrees of subdivision in a given dispersion medium. As an example may be cited a series of carefully studied aqueous gold dispersoids investigated by R. Zsigmondy.[1]

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[1] These figures are taken from a table on p. 64 of the excellent publication of W. Mecklenburg, Die exper. Grundlegung der Atomistik, Jena, 1910. The various methods of calculation may also be found there.

[2] See, for example, the summaries of G. H. Washburn, Jahrb. d. Radioaktivität, **5**, 493 (1908); **6**, 69 (1900).

[3] The Svedberg, Stud. z. Lehre v. d. koll. Lösungen. Nov. Act. R. Soc. Scient. Upsaliensis, Ser. IV, II, 1 (1907).

TABLE 2.—AQUEOUS GOLD DISPERSOIDS OF DIFFERENT DEGREES OF DISPERSION

Designation of the solution*	Color of the dispersoid	Calculated average size of particles in $\mu\mu$	
Au_{87}^{a}	Rose	About	6.0
Au_{92}	Bright red	About	10.0
Au_{97}	Bright red		15.3
Au_{92}^{b}	Bright red		17.0
Au_{91}^{a}	Violet red	About	23.0
Au_{83}^{a}	Violet red		32.0
Au_{2}	Purple red		38.0
Gold suspension *a*	Violet red		45.0
Gold suspension *b*	Bright red		95.0
Gold suspension *c*	Bluish		130.0

*The designations are those of Zsigmondy (*l.c.*).

Zsigmondy and other investigators have prepared gold dispersoids in which the size of the particles could not be determined. They must therefore have been smaller than $6\mu\mu$.

This variability in the degree of dispersion *within* the limits characteristic of colloid solutions has been recognized in the literature of colloid-chemistry by distinguishing between substances having a "*strong or a weak colloidality*," and different "*degrees of colloidality*." Substances have also been designated as systems "*slightly, intermediately, highly, or completely colloid*," or "*coarsely disperse, finely disperse*," etc. The term highly colloid is synonymous with highly disperse, etc. It is also at times advisable to distinguish between *supermolecularly dispersed* phases (as in the case of ions) and *submolecularly dispersed* phases.

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[1] R. Zsigmondy, Zur Erkenntnis d. Kolloide, 104, Jena, 1905.

The following outline gives graphically a classification of the dispersoids according to their degree of dispersion.

DISPERSOIDS

True or coarse dispersions (suspensions, emulsions, etc.).	Colloid solutions.	Molecular and supermolecular dispersoids (solutoids).[1]
Size of the particles of the disperse phase greater than 0.1μ.	Size of the particles of the disperse phase between 0.1μ and 1$\mu\mu$.	Size of the particles of the disperse phase about 1$\mu\mu$ or less.
Specific surface $<6.10.^5$	Specific surface between 6.10^5 and 6.10^7.	Specific surface $>6.10^7$.

→

Colloidality decreases

→

Degree of Dispersion increases

P. P. von Weimarn[2] has repeatedly emphasized that the so-called "*supersaturated solutions*" (in which we are justified in assuming the existence of larger molecular aggregates) occupy a position between the colloid and the molecular disperse-systems. But there seems to be no reason for believing as von Weimarn does that supersaturated solutions always represent transitions between colloid and molecular-disperse systems; or for believing that such transition types must appear every time we pass from a high degree of dispersion to a lower one or *vice versa*. The concept of supersaturation embodies in itself *no* information regarding degree of dispersion which alone is the criterion for the type of classification here under consideration. Supersaturation constitutes a possible but not the sole means of preparing submolecular dispersoids. Such may be prepared by "direct methods of dispersion."

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[1] This name was proposed by P. P. von Weimarn, Koll-Zeitscher, **7**, 155 (1910). It should be noted that von Weimarn wishes the terms "colloid," "colloid solution," etc., avoided and replaced by the more general terms "dispersoid" "dispersed solution," etc., while the term "colloid chemistry" is to be replaced by "dispersoid chemistry." In spite of the fact that I was the first to propose the extension of the study of the colloids to that of the disperse systems and first suggested a suitable nomenclature, yet, for obvious reasons I do not deem it advisable to eliminate the use of the term "colloid." Even the fact that the word "colloid" originally had a different meaning, namely, a more special one than it now has, does not justify the proposed measure. The word "molecule," for example, has not disappeared from science even though its exact meaning has changed frequently and considerably. A dispersoid chemistry, in other words, a chemistry dealing with disperse systems of all degrees of dispersion, does of course exist. Nevertheless, persistence in the use of the term colloid for at least that portion of this more general science with which this work deals seems to be justified on historical and other grounds. See my preface to the second German edition of this work.

[2] See P. P. von Weimarn, Koll.-Zeitschr., **6**, 179 (1910); and for greater details Kolloidchem. Beihefte, **1**, 331 (1910).

3. Defects of this Principle of Classification.—The following should be noted regarding the classification of the dispersoids according to their degree of dispersion.

The degree of dispersion is manifestly a *continuously* variable quantity, and so it is self-evident that it may have any possible value between the extremes which characterize individual classes of dispersoids. As a matter of fact, transitional values between those which characterize the field of colloid solutions and those which characterize the molecular dispersoids, or between those of the former and those of the coarse dispersions are not only conceivable but have been demonstrated experimentally. The existence of transitional values may be deduced from Table 2, for at its top are gold dispersoids with particles approaching molecular values in size, while at its bottom are suspensions which can be resolved under the microscope. An analogous series of dispersoids in which the degree of dispersion varied between points lying beyond *either side* of the field embraced by the colloid solutions was, among others, prepared by H. Picton and S. E. Linder[1] at an early period in the history of colloid-chemistry. Dispersoids of arsenious trisulphide in water were used. The size of the particles in these could not be determined directly, but that their degree of dispersion varied greatly was clearly demonstrated by their different degrees of diffusibility.

In the face of these facts it must be admitted that the classification of the dispersoids according to their degrees of dispersion is an *arbitrary* one. But while this is so, there is undoubtedly a practical justification for the distinctions proposed. The dispersion values given were chosen because with changes in them *abrupt* changes occur in other properties of the dispersoid also. Thus the particles of a dispersoid with diameters of less than 0.1μ are not only no longer visible under the microscope, but at this degree of dispersion they tend to show diffusibility and they no longer settle out spontaneously. On the other hand while these particles do not pass through a dialyzing membrane, produce no changes in the freezing and boiling points of their dispersion medium, etc., all these properties alter in value, greatly and suddenly, when molecular dimensions are approached. These *dis*continuous changes of *other* properties therefore form the true basis for the classification of the dispersoids on the ground of their degree of dispersion. But that a quantitative characterization of the dispersoids according to their degree of dispersion is important is evidenced by the fact that dispersion in itself must be regarded as the chief characteristic of the substances with which this book deals.

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[1] H. Picton and S. E. Linder, J. Chem. Soc., **61**, 148 (1892); *ibid.*, **67**, 63 (1895).

4. Polydispersoids.—It has frequently been found in determining the degree of dispersion in dispersoids, such as colloid solutions, that the individual particles of the disperse phase are of different sizes, in other words the degree of dispersion of the disperse phase must be described as *multiple*. According to L. Michaelis,[1] examples of such systems are found in the aqueous solutions of certain dyes, such as fuchsin, methyl violet, etc. In these there is a molecular-disperse phase in addition to a phase observable under the microscope or ultra-microscope. Many protein solutions probably behave in an analogous way, as may be inferred from their behavior on ultrafiltration (see later); but even the individual, ultramicroscopically observable particles in dispersoids (as in those of gold) are frequently of different sizes. It follows therefore that in practice we can only speak of an *average* dispersion value. The importance of the simultaneous existence of particles of different sizes in one and the same dispersion medium for many questions of colloid-chemistry, for example in that of their stability, will be discussed in detail later.

These systems in which the disperse phase is composed of particles having different degrees of dispersion may be called *polydisperse systems or polydispersoids.*

5. Dispersoids Varying with Changes in Concentration.—In a number of molecular as well as colloid dispersoids the remarkable fact has been observed that *the degree of dispersion varies progressively with changes in concentration.* In all the cases thus far studied it decreases with increasing concentration. Cane sugar, for example, in dilute solution has all the typical attributes of a molecular dispersoid. But when cane sugar solutions of higher concentrations are investigated by applying the Tyndall test to them it is found that they show an intense light-cone this proving themselves submolecularly disperse. Entirely analogous observations have been made on solutions of various salts such as aluminium sulphate, and on those of certain dyes, proteins, etc. No doubt careful investigation will demonstrate the wide-spread nature of this remarkable fact. It should be added that such a progressive decrease in the degree of dispersion by simply changing the quantitative relations of the dispersoid to the dispersion medium may be demonstrated by yet other than purely optical methods. Further details will be given in discussing the individual physico-chemical properties of the colloids especially in the chapter on their internal changes of state. Analogous phenomena are encountered in studying the properties of molecularly and supermolecularly dispersed systems, being then described as "polymerizations, condensations," etc.

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[1] L. Michaelis, Deutsche medizin. Wochenschr, Nr. 24 (1904); Virchow's Arch., 179, 195 (1905).

We will call these systems, among which many colloid dispersoids appear, "*concentration-variable systems*."

6. Temperature-variable Dispersoids.—Just as the degree of subdivision of a dispersoid may vary with changes in concentration, it may also vary with changes in temperature. As far as we know now, raising the concentration of a dispersoid produces the same type of change as lowering its temperature. A disperse system therefore tends to become *less* disperse when the temperature is lowered. Such anomalous behavior in "true" solutions has generally been explained by saying that the substances "polymerize" or "condense."[1] An analogous behavior, resulting in diminutions of degree of dispersion, is found in even greater degree in colloid systems. Here we can only point out the fact; it is to be dealt with in detail in the chapters on internal changes in state, more particularly in that on gelation.

Dispersoids showing this property are called "*temperature-variable dispersoids*."

7. Complex Dispersoids.—There exists another class of complex systems which is interesting for both the theory and the practice of colloid-chemistry. It is characterized by the fact that *each constituent of such systems, both disperse phase and dispersion*

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[1] For examples and literature see H. Schade, Koll.-Zeitschr., 7, 26 (1910).

medium, is in itself a dispersoid. Evidently the degree of dispersion in these individual dispersoids must *always be higher* than that of the compound dispersoid. And in fact, the best-known examples of such systems are those in which the individual dispersoids have a molecular degree of dispersion, while the compound dispersoid is colloid or molecular-disperse in character.

The best examples of such "*complex dispersoids*" are found among the emulsions, that is among those systems in which both phases are liquid. Pretty instances are formed by the so-called *critical mixtures of liquids* and their analogues. As is well known, it is possible at suitable concentrations and at suitable temperatures to make a dispersoid of two liquids which have a limited molecular solubility in each other. As an example may be quoted the production of an emulsion of phenol in water. Since all liquids are mutually soluble to some extent at least, this type constitutes the bulk of the dispersion systems having a liquid-liquid composition. Such complex dispersoids are characterized by the fact that *changes in the concentration or in the temperature of the macrodisperse system are accompanied by changes in the composition of the microdispersoids.* Thus when droplets of phenol are dispersed in water, both phases contain phenol as well as water. If the concentration of the emulsion is changed through the addition of one of its components, for example water, the composition of both microdisperse phases is also changed. As more water is added the phenol phase becomes progressively richer in water until a limit is reached (until the phenol is *saturated* with water), etc. Variations in temperature produce analogous effects.

Another peculiarity of these complex dispersoids which should be emphasized is that in addition to the fact that the composition of the individual phases changes with variations in concentration or temperature, their *degree of dispersion* does also, and apparently whenever a change is produced in the total concentration. Thus the droplets in mixtures of liquids of limited mutual solubility become progressively smaller as the mixtures approach the so-called critical concentration, and disappear altogether at the "critical point;" in other words, the droplets become molecular-disperse. But at constant temperature the critical concentration is always less than the concentration of the fluids in a coarsely disperse state. Here again there exists exactly the same variation in degree of dispersion with change in concentration that was previously described.[1]

What was said above regarding simple dispersoids holds for the influence of temperature on composition and degree of dispersion in complex dispersoids also. *The complex dispersoids are concentration-variable and temperature-variable systems.*

Dispersoids with a liquid dispersion medium and a *solid* disperse phase may also form complex systems, but up to the present time these have been studied but little. It is self-evident that a solid particle floating in a liquid may either take up part of it *into itself*, or attach a layer of it *to itself*. Such behavior may be observed macroscopically when solid gelatine is pulverized and thrown into cold water. Each particle then "swells," that is, it absorbs water, but if the temperature is low enough it does not lose entirely the properties of a solid. But the properties of a solid, such as constancy of form and elasticity, become less marked as the solid particles take up more water or as the temperature rises. This very important behavior, which therefore consists in an approximation of the previously solid state to that of a liquid, will be discussed in detail later (see page 44).

Let it further be pointed out that complex dispersoids may be expected to appear more frequently in systems composed of two liquid phases than in those composed of a liquid and a solid phase. This depends upon the fact that a greater mutual molecular miscibility may be assumed to exist in the case of two liquids than in the case of a liquid and a solid phase, and second, upon the fact that the "solubility" of two liquids is *mutual. Both* phases will therefore be disperse in a liquid-liquid dispersoid. On the other hand, while we may be able to speak of the "solubility" of a solid phase in a liquid dispersion medium we shall only rarely be able to speak of the "solubility" of the dispersion medium in the solid disperse phase.

It seems of interest to mention in this connection that many reasons have recently been found for assuming the existence of similar phenomena in molecular and ionic dispersoids. Such complexes are called "solvates," or if they occur in aqueous solutions, "hydrates." In these compound disperse phases there also occur variations in composition with changes in concentration or in temperature entirely similar to those discussed above.

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[1] It should be noted that concentration is always regarded as the quotient of the amounts of the $\frac{\text{disperse phase}}{\text{dispersion medium}}$. In the range *above* the critical point this fraction is reversed, in that the dispersion medium becomes the disperse phase and *vice versa.*

8. Transition Phenomena.—The transition phenomena observed in passing from the members of one class of dispersoids to those of another having a different degree of dispersion are particularly interesting. Our knowledge of the properties of dispersoid systems is at present distributed in such a way that we may say we know a great deal about typical molecular dispersoids, somewhat less about typical colloids, and still less about typical coarse dispersions. But the atypical representatives of all three classes, that is, the transition forms between coarse dispersions and colloids on the one hand, and between colloids and molecular dispersoids on the other, have been almost entirely neglected. There is an historical reason for this state of affairs. As is well known, the founder of colloid-chemistry, Thomas Graham, was so impressed by the differences between typical colloids and typical molecular dispersoids that he declared the two to represent "different worlds of matter." He endeavored in consequence to contrast them as much as possible. The majority of his successors followed him in this, and only recently has the effort been made to cease discovering rare and sharp *distinctions* between colloids and molecular dispersoids. As a matter of fact no such sharp distinctions exist. But the realization of this fact was important in that it yielded a new point of view, on the basis of which it became possible to formulate the concept of the dispersoid, and with it to obtain a rational systematization of these bodies[1] (see later). It must be emphasized, however, that even today comparatively few investigations are carried out with the conscious purpose of studying these transition phenomena, more especially the changes which the individual physical and physico-chemical properties exhibit with progressive variations in the degree of dispersion.

§7. General Colloid-chemical Nomenclature

Dispersoids are called sols if they have the properties described in the foregoing paragraphs, if their degree of dispersion lies between 6.10^5 and 6.10^7, and the disperse phase is uniformly distributed throughout the dispersion medium. This name originated with Thomas Graham.[1] When we speak of "a colloid" we nearly always mean one in this condition, in other words, one in the *sol condition*. There exists also what Graham first called the *gel condition*. A sol becomes a gel when its degree of dispersion is decreased in such a way that it passes beyond the lower limits characteristic of the colloids, in other words, when the system becomes *microscopically* heterogeneous. A usual, though not an absolutely necessary accompanying phenomenon of gel formation is a loss of the uniform distribution of the disperse phase in the dispersion medium. The sol "*precipitates*," "*clots*," "*coagulates*," "*cements*," etc. It is sometimes said that the sol "*gelatinizes*," but it is best to reserve this word for another process which can be distinguished from the ordinary "*precipitation*," "*clotting*," or "*coagulation*."

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[1] See Wo. Ostwald, Koll.-Zeitschr. 1, 291, 331 (1907).

The phenomena opposed to "coagulation," in other words, those which result in an increase of the degree of dispersion and tend toward an approximately or absolutely uniform distribution of the disperse phase in the dispersion medium are summed up under the term "*peptization*." This term was also first suggested by Graham. All variations in the degree of dispersion and in the properties connected with it are designated by a term introduced by Wolfgang Pauli—"*changes of state in colloid systems*." When a change in the state of a colloid may be reversed by reversing the conditions which brought that change about, it is said to be "reversible." Thus when a colloid which has been precipitated by a salt goes back into solution on removal of the salt, the colloid change is said to be "reversible." On the other hand, if this does not occur it is "irreversible." The reversibility of such a change of condition is *not* determined, in the main, by the nature of the colloid itself, but rather by the character of the conditions which produce the coagulation. Thus the precipitation of typical protein sols by neutral salts is reversible, but their precipitation by heat is irreversible. We cannot therefore speak of reversible and irreversible *colloids*, as is still frequently done, but only of reversible and irreversible *changes in state* in the colloids. Another inappropriate word is "*solid-sol*," by which is really meant a gel which will redissolve in the dispersion medium from which it has been precipitated or dried.

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[1] Th. Graham, Phil. Trans. Roy. Soc. (1861); Liebig's Ann., **121**, 1 (1862).

According to the chemical name of the dispersion medium we also distinguish between *hydrosols* and *hydrogels*, alcosols (alcohol-sols) and alcogels, sulphosols (sulphuric acid sols) and sulphogels. If the dispersion medium is an organic liquid, the dispersoid is called an organosol, etc. The chemical name of the disperse phase is used as a prefix, thus: gold-hydrosol, silicic acid-alcogel, ice-xylosol, etc.

CHAPTER II

RELATIONS BETWEEN THE PHYSICAL STATE AND THE GENERAL PROPERTIES OF COLLOID SYSTEMS

§8. Classification of Dispersoids According to the State of Their Phases

1. The Physical State of the Disperse Phase as a Principle of Classification.—As soon as we attempt to carry out practically the classification of the dispersoids an the basis of their degree of dispersion we find that this principle does not always suffice. Two dispersoids, for example, may be identical in that the size of the particles of their disperse phases is the same, yet their other properties may differ so widely that the similarity appears as a mere incident. This may be illustrated by the great difference between a quartz or kaolin suspension in water and an emulsion of oil in water even when the average size of the particles in the two is the same. But for the colloids in particular such a classification according to degree of dispersion seems to be entirely inadequate. First, the extremes between which the degree of dispersion may vary in colloids are not widely separated. According to the classification of Zsigmondy the degree of dispersion in colloids can only vary between 6.10^5 and 6.10^7 while that of coarse dispersions and molecular and supermolecular dispersoids is limited on one side only. Second, different colloid solutions are known in which the particles are of the same size, but which in other points differ so markedly from each other that the similarity in degree of dispersion seems merely accidental or unimportant. What we need therefore is an additional principle of classification which is not based upon the size of the particles. Such an one lies close at hand.

Since colloid systems are heterogeneous or polyphasic—a fact discussed in detail in the preceding chapter—we may use the physical character (the physical state) of the phases composing the systems as a basis for classification. We may classify dispersoids according to the character of their phases quite as justly as according to the number or the degree of dispersion of their phases. Theoretically, such a classification would be as valuable as the other two. But when we consider that an entire series of properties changes, whenever the physical character of a phase changes, a classification based on this character is evidently a more natural one than that based upon any arbitrarily chosen *single* property. The succeeding paragraphs will show that a classification of dispersoid systems, more particularly of colloid systems, according to the physical state of their disperse phases is at least as important as their classification on the basis of their degree of dispersion.

2. Classification of the Dispersoids According to the Physical State of Their Phases.—The most important dispersoids that need to be considered are diphasic. By joining the three physical states of matter in pairs we obtain the following possibilities:

1. Solid + Solid.
2. Solid + Liquid.
3. Solid + Gas.
4. Liquid + Solid.
5. Liquid + Liquid.
6. Liquid + Gas.
7. Gas + Solid.
8. Gas + Liquid.
9. (Gas + Gas.)

No example exists of a dispersoid having the composition Gas + Gas, for gases are freely and completely miscible with each other in all proportions. Examples of the other classes are:

1. Solid + Solid.—Intercalations of foreign particles in many minerals (microliths, etc.), carbon particles in iron, of coloring matter in mineral salts and precious stones; "solid" colloid solutions, mixed crystals, solid solutions.

2. Solid + Liquid.—Liquid intercalations in many minerals, water of occlusion, inclusion and crystallization.

3. Solid + Gas.—Gaseous inclusions in many minerals (meerschaum, pumice stone, lava, tufa), solutions of gases in solids (hydrogen in iron, etc.).

7. Gas + Solid.—Smoke, for example tobacco smoke; condensing metallic vapors (F. Ehrenhaft); cooling vapors of ammonium chloride; cosmic dust, etc.

8. Gas + Liquid.—The fog formed at the liquefaction point of gases or in the condensation of steam; atmospheric fog, clouds, Tyndall's photochemically produced liquid fog, etc.

All these will be discussed in detail later.

The classes of dispersoids mentioned under 4, 5, and 6 are by far the most important and deserve special attention in colloid chemistry. The dispersion medium is liquid in all three cases, the disperse phase is solid in the first instance, liquid in the second, and gaseous in the third. The most familiar examples of these three classes of dispersoids are the coarse dispersions known as *suspensions*, *emulsions*, and *foams*.

§9. Transition Phenomena. Complex Dispersoids

1. General Considerations. Influence of Temperature and Degree of Dispersion.—As soon as we study the problem closely, it becomes evident that *transitions* are encountered in this scheme of classification also. This is more particularly true in passing from the solid to the liquid state, a transition which is produced more frequently and more easily, as is well known, than the transition from liquid to gas. Thus one and the same dispersoid may be an emulsion or a suspension, depending upon the temperature. At ordinary temperatures a few drops of an alcoholic mastic solution or of an alcoholic solution of rosin form a suspension when poured into an excess of water, but if the system be heated to the melting point of the resins a mixture of two liquid phases or an emulsion results. Between these two temperatures all possible transitions between solid and liquid may appear. In the last analysis the difficulty of drawing a sharp line between suspensions and emulsions is identical with the more general one of formulating a precise definition of the solid as contrasted with the liquid state of matter. Since the discovery of liquid crystals and crystalline liquids the only criterion we seem to have left to characterize the solid state is its enormous internal friction.

When we deal with droplets of microscopic size, their liquid character [that is to say, the presence of free (positive) surface energy in them] can be demonstrated rather easily by deformation experiments. But it is much harder to ascertain the physical state of a disperse phase when higher dispersion values come into play. As E. Hatschek[1] has shown particularly well, the amount of energy necessary to produce the deformation of a liquid droplet increases very rapidly with increase in degree of dispersion.

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[1] E. Hatschek, Koll.-Zeitschr., **7**, 81 (1910).

While its own weight suffices to squeeze a macroscopic oil globule through a glass tube half its own diameter a pressure of 4.5 atmospheres is necessary under analogous experimental conditions if the oil droplet is 0.2μ in diameter. Such a drop is still visible under the microscope. The explanation for this lies in the great increase in the surface energy of a given volume with its progressive subdivision. (For details see later.) *The greater the degree of subdivision of a liquid disperse phase, the more does it approximate a solid in its mechanical behavior.*

P. P. von Weimarn,[1] starting with other, mainly moleculo-kinetic, conceptions, has reached a conclusion the converse of this. The properties of *solid* disperse particles approach those of a *liquid* as their degree of dispersion increases. We may say, therefore, that *differences between liquid and solid disperse phases become progressively less marked as the degree of dispersion increases.* In entire agreement with this conclusion is the fact that the importance of the original physical state disappears entirely when the phases become molecular-disperse. Thus all solutions of acetic acid are the same whether they are prepared from the vapor or from the liquid or solid forms of acetic acid.[2]

2. Influence of Concentration upon State in Complex Dispersoids.—Further analysis shows that in addition to temperature and degree of dispersion the *concentration*, that is to say the quantitative relation of the components of a dispersoid to each other, may have an important influence upon its state. Two possibilities may be distinguished:

1. The state of the dispersoid as a whole may vary with the concentration.

2. The state of the *individual* phases of the system may vary with the concentration.

We seem at first sight to deal here with rare and complex phenomena, but while it is true that only suggestions of them are found among the best-known dispersoids, namely the molecularly and coarsely disperse, they play an important part in certain colloids. Let us first consider the behavior of the simpler dispersoids of this type when their concentration is varied.

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[1] P. P. von Weimarn, Koll.-Zeitschr., **6**, 32 (1910); **7**, 155 (1910).

[2] It is therefore impossible and so purposeless to try to distinguish molecularly disperse systems (solutoids) from each other on the basis of the "solid" or "fluid" nature of the disperse phase as P. P. von Weimarn (*l.c.*) proposes. But this statement is not to be construed as meaning that the processes of formation or of solution are identical in the two cases. The heats of solution are certainly different. Since in a classification of disperse systems we only classify the like results of very different physical and chemical processes, the advantage of utilizing these differences in modes of preparation for purposes of classification is not evident.

(*a*) The state of a molecular-disperse solution is determined by the state of the solvent. The reason for this is that the original state of the dissolved substance has lost its importance when a molecular-disperse phase results, as already explained above. In the case of those atypical solutions which are more or less solid, there are good reasons for supposing that in them the disperse phase has not remained in a molecular state of subdivision, but has been polymerized, associated or condensed into submolecular and then into colloid particles, as discussed above. Thus soap solutions are molecular-disperse *and* liquid in low concentrations, but are colloid *and* solid in higher concentrations. If the concentration is varied while the molecular degree of dispersion is maintained a separation of the disperse phase in liquid or solid form generally occurs, in other words saturation is attained.

(*b*) The state of a coarsely disperse system depends in an interesting way upon concentration. In certain *extremes of concentration*, bodies having a liquid dispersion medium and a gaseous, liquid, or solid disperse phase may assume some of the properties of solids, such as constancy of form and elasticity. Solid powders mixed with a little water illustrate this. Sand with a definite but by no means immeasurably small water content may be cut into slices. Emulsions of mineral oil in soap, or of water in mineral soaps form stiff pastes in certain concentrations;[1] if the concentrations are slightly changed a coarse mixture of liquids is again formed which may be poured from one vessel to another. As is well known, foams prepared with small quantities of a liquid dispersion medium may have a definite shape and exhibit considerable solidity. Thus, a slice of pasteboard weighing two grams will not sink into a well-whipped saponin foam.

It is characteristic of all these systems that they contain a great excess of the disperse phase, though even here an optimum concentration exists beyond which the system again loses its solid state.[2] In these "*highly concentrated dispersoids*" the dispersion medium surrounds the disperse phase with a "liquid film" which deprives the disperse particles of their mobility, and so imposes upon them the properties of a solid.

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[1] See S. U. Pickering, Koll.-Zeitschr., **7**, 11 (1910); D. Holde, *ibid.*, **3**, 270 (1916).

[2] See Wo. Ostwald, Koll.-Zeitschr., **6**, 185 (1910).

(*c*) Particularly interesting and important phenomena appear among the *complex* dispersoids. The more important characteristics of these bodies, such as variations in concentration in the individual dispersoids with temperature and total concentration, and variations in the degree of dispersion with the same factors, were mentioned above. In considering the influence of concentration on the state of complex dispersoids we have therefore to deal with an exceptionally large number of factors which may all act in the same general direction but some of which may also counteract others.

A. COMPLEX SYSTEMS HAVING THE COMPOSITION LIQUID + LIQUID

(*a*) **Influence of Concentration upon the State of the Dispersoid as a Whole.**—In Liquid + Liquid systems the same influence of concentration described above for simple, coarsely disperse suspensions may exhibit itself, and a body having the properties of a solid may result. Here also a sudden "setting" may take place in certain limited regions of concentration. But to this there must be added the influence of the total concentration not alone upon the concentration of the *individual* dispersoids, and *consequently upon their physical properties*, but also upon the *degree of dispersion* of the system *as a whole*, and thus upon its state. If we try to imagine what must be the effect of these individual factors upon the behavior of such complex dispersoids we can only suspect that the changes in state of the system as a whole with changes in concentration or temperature must be smoother in the case of the complex dispersoids than in the case of the simple ones. For, generally speaking, it is probable that the consequences of any change will manifest themselves less clearly when a great number of factors working partly in the same, partly in opposite directions, are affected by it than when only one or a relatively small number of such determining factors are affected. This is particularly true of systems that occupy an intermediate position among the dispersoids, in other words of the colloids. It follows from *the principle of continuity* which justly plays a great rôle in all science that colloid systems having the composition Liquid + Liquid must occupy an intermediate position between coarse dispersions and molecular dispersoids in this respect also.

(*b*) **Influence of Concentration on the State of the Disperse Phase.**—Exceptionally complicated and interesting relationships become apparent when we take into consideration the fact that in complex systems the state of aggregation of one of the individual dispersoids, the disperse phase for example, may be changed in the same way as that of the compound dispersoid by a change in concentration. For there is no reason for excluding the possibility that a floating droplet having the composition Liquid + Liquid may "set" in certain concentrations and at certain temperatures as does the dispersoid as a whole at other concentrations, perhaps. Just as soap, water, and paraffin oil may form a body having the properties of a solid under certain conditions, so a disperse particle having a similar composition may suddenly stiffen even though the dispersion medium itself may still be liquid. A great variety of possibilities exists here which we shall encounter again later.

B. COMPLEX DISPERSOIDS HAVING THE COMPOSITION LIQUID + SOLID

(*a*) **Influence of Concentration on the State of the Dispersoid as a Whole.**—It is easily seen that when a complex system has the composition Liquid + Solid (a suspension of swollen gelatine particles, for example) it may assume the properties of a solid as its concentration rises. There need only be enough particles in a given volume of liquid so that in the process of swelling they interfere with each other's movement in order to get a stiff jelly. Figuratively speaking, the particles at higher concentrations struggle with each other for the dispersion medium, and as the amount of liquid at their disposal decreases the particles adhere more and more firmly to each other. This may be observed experimentally if the liquid dispersion medium is gradually removed by evaporation. In this way a typical solid is finally obtained.[1] Conversely, such a complex system will tend to approach a normal liquid in character as the number of suspended particles contained in the unit volume is lessened. If the dispersion medium is also heterogeneous, that portion of it which is made up of the disperse phase must also increase when the total concentration is increased so that the augmented viscosity resulting from this will further aid in giving the dispersoid as a whole a solid consistency

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[1] The crystalline structure of solid bodies is disregarded here.

(*b*) **Influence of Concentration on the State of the Disperse Phase.**—The state of the solid disperse phase more nearly approaches that of a liquid the greater the amount of dispersion medium it has absorbed.

To sum up we may say that a great variety of relations exists between the state of the individual phases composing the dispersoid and its general properties. Of greatest significance is the fact that *a system having the properties of a solid may be formed from a disperse mixture of non-solid phases.* Other disperse systems having the composition Gas + Solid or Gas + Liquid may assume the properties of *liquids.* Thus smoke or fog sometimes exhibit phenomena of (positive) surface tension ("rings" of smoke); and at least most of the *hydrostatic* properties of liquids may be easily demonstrated in *extremely concentrated* systems of this composition, as in not too fine, dry sand.

§10. Colloid Systems as Suspensoids and Emulsoids

1. General Considerations.—Once we accept the physical heterogeneity of colloid systems we are compelled to consider the state of their phases. The dispersoids that must first be dealt with are those which have a liquid dispersion medium. Special attention must therefore be paid to the part played by the state of the *disperse* phase.

In considering the three types of systems which belong to this group we may disregard the class Liquid + Gas, for these (foams composed of extremely small bubbles) are not typical representatives of the colloids. This should not be taken to mean that such systems are unknown or are incapable of existing. The turbidity which appears in liquids about the critical vaporization point is probably dependent upon the formation of a great number of gas bubbles in a high degree of dispersion. A detailed comparison of the properties of these systems with those of others has not been made as yet, although their optical behavior, the effect of the walls of the vessels containing them, etc., demonstrate the close relationship of these to the dispersoids. A detailed theoretical and practical study of the whole problem, more especially of the critical cloudiness of liquid mixtures, would yield fruitful results, for great similarities have already been shown to exist between these systems and certain colloids (see later).

We have therefore to concern ourselves only with colloid solutions having the composition Liquid + Solid and Liquid + Liquid. According to our classification we may expect to encounter *two* classes of colloids, and our problem narrows itself down to the relations existing between suspensions and emulsions on the one hand and colloid solutions on the other. On *a priori* grounds it would seem possible that the coarse dispersions mentioned might yield two types of colloid solutions when the degree of dispersion is properly increased. The question as to what properties such systems exhibit is worth our attention.

2. The Empirical Establishment of Two Classes of Colloids.—The existence of two classes of colloids differing markedly from each other has recently become apparent on purely empirical grounds and entirely independently of any theoretical considerations. Protein and gelatine solutions represent one extreme, Zsigmondy's aqueous gold dispersoids the other of these two types of colloid solutions. Different names are employd in the literature for these two sets of colloids, different investigators having made use of different properties for their characterization. V. Henri[1] calls them "stabile" and "instabile" colloids, A. A. Noyes,[2] "colloidal solutions" and "colloidal suspensions," J. Perrin,[3] "hydrophilic" and "hydrophobic" colloids, and also "hydrosoles stables et colloides hydrophiles." After Wolfgang Ostwald[4] pointed out that the latter names are too narrow since the character of the dispersion medium may vary, H. Freundlich[5] and W. Neumann suggested the more comprehensive terms "lyophilic" and "lyophobic" colloids. All these terms are either based upon the existence of some striking individual difference between the two groups or else are expressive of particular theoretical conceptions. Noyes has analyzed the two classes of colloids from a broad experimental point of view. He characterizes one type as "*viscous, gelatinizing, colloidal mixtures not (easily) coagulated by salts*," the other as "*non-viscous, non-gelatinizing, but easily coagulable mixtures*." A possible addition to Noyes' happy empirical description is that the former usually have a *lower surface tension* than their pure dispersion medium, while in the latter the tension is practically unchanged. Further, *electrical factors* usually play a more important rôle in the latter than in the former. This is evidenced, for example, by the great precipitating power which polyvalent ions have upon the non-viscous colloids.

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[1] V. Henri, Zeitschr. f. physik. Ch., **51**, 29 (1905).
[2] A. A. Noyes, Journ. Amer. Chem. Soc., **27**, 85 (1905).
[3] J. Perrin, J. Chim. Phys., **3**, 50 (1905).
[4] Wo. Ostwald, ZKoll.-eitschr., **1**, 291, 331 (1907).
[5] H. Freundlich and W. Neumann, Koll.-Zeitschr., **3**, 80 (1908).

Examples of the "non-viscous, etc.," colloids are the metallic sols, sulphide sols, many dyes (congo-red for instance), iron hydroxide in *dilute* solution, etc. The best illustrations of the other class are: the proteins and related substances, gelatine, agar, cholesterol, silicic acid, "meta"-phosphoric acid, stannic acid, meta-hydroxides in *concentrated* solution, so-called gelatinous salts (sulphates, phosphates, carbonates, etc.), dye-stuffs like night-blue, etc.

The question now arises whether these two classes of colloid solutions do actually represent dispersoids having the composition Liquid + Solid and Liquid + Liquid.

3. The Theoretical Characterization of the Two Classes of Colloids.—Even the theoretical conceptions which led to the use of the expressions "lyophilic" and "lyophobic" imply the existence of a close relationship between the properties denoted by these names and the state of the disperse phase. This is particularly true of the "lyophilic" colloids which we characterize as systems having the composition Liquid + Liquid, for when we say that the disperse phase is here composed of "exceedingly swollen particles" or of "particles united to a great number of liquid molecules," we imply that its state is liquid. Statements like this of J. Perrin:[1] "Un granule d'hydrosol stable contiendrait une très forte proportion d'eau, 90 percent par exemple" can hardly be interpreted differently. Yet while such statements may be regarded as approaching a characterization of the two classes of dispersoids on the basis of the state of their disperse phases, a detailed analysis of these two classes based on experimental study has been attempted only recently. This is particularly true of the "lyophilic" colloids. The colloids described as "lyophobic," "unstable," etc., were characterized as dispersoids having the composition Liquid + Solid early in the history of colloid-chemical investigation as an almost self-evident conclusion to be drawn from a consideration of their properties. The similarities between colloid metals, for example, and coarse dispersions having the composition Liquid + Solid are so great and the relations between them so intimate and striking that even before the formulation of the concept of "colloidality,"[1] B. J. Richter,[2] M. Faraday,[3] and J. Berzelius[4] thought of the former as suspensions of particles of the same character as "reguline" metals. B. J. Richter showed as far back as 1802 that gold in its well-known "aqueous solutions" does not exist here in some unknown molecular condition, but in a finely divided *metallic* (solid) state. This conclusion was afterwards confirmed by Faraday and Zsigmondy, and extended to other colloids of this group by other investigators.

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[1] J. Perrin, J. Chim. Phys., **3**, 84 and 87 (1905).

We might now try to correlate these two empirically established types of colloid systems with the dispersoids having the composition Liquid + Solid and Liquid + Liquid by detailing the similarities between the two sets of systems. But such a comparison would presuppose knowledge of a great number of the special properties of colloid systems which only the succeeding portions of this book will bring. The results of comparison would not be convincing, for the facts to be employed could only be pointed out here in brief. We shall therefore *for the present* only *assume* that the two types of colloid systems under discussion differ from each other in the matter of the state of their disperse phases and in the properties which result from this fundamental difference. We shall of course not disregard the necessity of proving this assumption later.[1]

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[1] Wo. Ostwald, Koll.-Zeitscher., **1**, 291, 331 (1907). The statement of A. Müller, [Allg. Chemie d. Koll., 147, 186, Leipzig (1907)], that G. Quincke [Ann. d. Physik. (4) **9**, 797, 1009, etc. (1907)] first classified colloids according to the type of the disperse phase is not correct. The statements of Quincke which no doubt led to this historical error, do not refer to colloid systems but to coarsely dispersed ones. Quincke holds all colloid solutions (including those of arsenious trisulphide) to be mixtures of two fluid phases (*l.c.*, 1009, 1034, etc.). See in this connection G. Bredig [Ann. d. Physik., **1**, 11, 221 (1903)].

[2] B. J. Richter, see Wilh. Ostwald, Koll.-Zeitschr., **4**, 5 (1909).

[3] M. Faraday, Philos. Mag. (4) **14**, 401, 512 (1859).

[4] J. Berzelius, Lehrb. d. Chemie, 2 Aufl., **2**, 244 (1823).

4. The Frequency of Occurrence of Complex Emulsoids.—Let us anticipate a particularly important *generalization* which follows from characterizing the "lyophilic" colloids as systems having the composition Liquid + Liquid. The behavior of such colloids demonstrates clearly the liquid character of the disperse phase in them and emphasizes, first, that the *"lyophilic" colloids are complex dispersoids*, that is to say, their individual phases are in themselves dispersoids of a higher degree of dispersion, and, second, that the composition of these individual dispersoids as well as their degree of dispersion varies greatly with concentration, temperature, etc. Further, in consequence of the complex character of these systems *the state of the disperse phase may pass progressively from liquid through semisolid to solid.* The possibilities of variation in the state of a complex dispersoid with degree of dispersion, temperature, concentration, etc., as discussed on p. 45, appear very clearly in these colloids and undoubtedly constitute one of the chief reasons why their behavior is so much more varied than that of colloids having the composition Liquid + Solid.[2] The value of this conception will also show itself in discussing the individual phenomena characteristic of these systems, when it will become evident that the different theoretical views held regarding the properties of these two classes of colloids may not only be correlated but be simplified and explained if the differences in the types of the disperse phases and the consequences thereof are kept in mind.

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[1] An exact classification and description of both classes of colloids according to the type of the phases was indicated in the first German edition of this book. Since then I have found only further and very excellent support for this view. I hope in the near future to publish a monograph on the physical theory of colloids of the composition Liquid + Liquid (see the following footnote).

[2] Even in the first German edition of this book (pp. 111, 328, 356, 374, etc.) I emphasized that lyophilic colloids are not "only" systems of the composition Liquid + Liquid, but also dispersoids of a "higher order," or, in the words used above, complex dispersoids. This has not been taken into account by those writers who have objected to my characterizations by pointing out that colloid mercury which consists of two fluid phases has no lyophilic properties. They have erroneously ascribed to me the view that all Liquid + Liquid systems have such properties, while actually I merely held the narrower opinion that lyophilic colloids belong to these systems. But it may be pointed out again that for the reasons given on p. 47, complex systems may be expected in systems of the type Liquid + Liquid with greater certainty than in those of the type Liquid + Solid. A complex composition is therefore more general and commoner in a Liquid + Liquid dispersoid. If colloids of the composition Liquid + Liquid were unknown it would be necessary to seek them and they would no doubt be easily found.

5. Relation of These Two Colloid Classes to Molecular Dispersoids.—Many investigators have pointed out that greater similarities exist between "lyophilic" colloids and typical molecular dispersoids than between the latter and colloids of the type Liquid + Solid. Without going into details which must be reserved for later, we may emphasize that such relations may be expected on the mere basis of our characterization of the "lyophilic" colloids as Liquid + Liquid systems. Physical chemists have recently become increasingly certain that the highly disperse phases of molecular and supermolecular solutions must be conceived of as combined with a number, sometimes a very considerable number (100 and more), of the molecules of the solvent as *solvates*. Even though, as emphasized before, we cannot speak of the state of aggregation of a molecule, such a union of solvent with molecule cannot be conceived of physically other than as a highly disperse liquid. As a matter of fact, recent workers on the theory of solution speak of "droplets."[1] This widespread impression of the existence of a closer relationship between "true solutions" and "lyophilic" colloids than between the former and "lyophobic" systems therefore corresponds with the conceptions above presented.

6. Suspensoids and Emulsoids.—In view of the relations existing between these two classes of colloids and the corresponding coarse dispersions it seems expedient to give the former special names. R. Höber[2] introduced the name *suspension colloids* for the colloids of the type Liquid + Solid. An analogous term for the second class would be: *emulsion colloids*. The abbreviations *suspensoids* and *emulsoids* have been suggested by P. P. von Weimarn.[3] These will be employed in the succeeding pages of this book. If one wishes to characterize a colloid in greater detail one may speak of "polysuspensoids" (systems composed of solid phases having different degrees of dispersion), of "complex emulsoids," etc. No objection can, of course, be raised against expressions like "lyophilic emulsoids." Only it should be remembered that the terms "suspensoids" and "emulsoids" in contradistinction to "lyophilic" and "lyophobic colloids" have the advantage of expressing more definite and hence more fruitful views regarding the properties of the dispersoids. A view which connects the state of the disperse phase with the general conception of the dispersoid seems incomparably more concrete, more useful, experimentally, and more suggestive than, for example, the conception of "lyophilia."

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[1] See K. Drucker, Zeitschr. f. physik. Chem., **67**, 634 (1909).

[2] R. Höber, Physik. Chem. d. Zelle., 2 Aufl., 208, Leipzig, 1906.

[3] P. P. Von Weimarn, Koll.-Zeitschr., **3**, 26 (1908).

§11. Transition Phenomena between Suspensoids and Emulsoids

As already mentioned, it is possible for a phase to pass smoothly from a solid to a liquid state and *vice versa*. Often such progressive changes may occur during the process of coagulation in one and the same system, as in a complex dispersoid. Thus an originally *liquid* disperse phase may be precipitated in an almost *solid* condition by appropriate means of coagulation. Such a transition from emulsoid to suspensoid demonstrates particularly well the properties which result from a change in the state of the disperse phase. According to J. Friedländer,[1] for example, two kinds of systems may be prepared from alcohol, rosin and water, both of which are turbid, thus proving them disperse heterogeneous systems. The first of these is made by pouring a few drops of an alcoholic solution of rosin into an excess of water when the rosin, which is practically insoluble in water, separates out as a *solid* disperse phase while the alcohol, in greater part at least, is dissolved in the water. The second is made by adding a few drops of water to a concentrated alcoholic solution of rosin. In this case the first drops of water probably dissolve in the rosin-alcohol, but further amounts can dissolve only in the alcohol or, perhaps, succeed in withdrawing this from the solution so that small droplets of water-alcohol (liquid) appear in the liquid, alcoholic solution of rosin and make it turbid. A disperse heterogeneous system with a *solid* disperse phase as well as one with a liquid disperse phase may therefore be prepared from the same three components by appropriate changes in their concentration. Friedländer found the behavior of the two systems to be entirely different. "Such a turbid mixture (a concentrated alcoholic solution of rosin to which a little water has been added) behaves very differently from the ordinary rosin suspension in that it is not coagulated by an increase in temperature or on the addition of electrolytes. When the temperature is lowered the rosin phase becomes solid but is not coagulated, for a rise in temperature restores the system to its previous condition. Although previously irreversible, the system is now completely reversible."[1] Friedländer further found the internal friction of the second kind of system to be greater than that of the first. In this respect the second system closely resembles typical emulsions such as those of isobutyric acid in water. A detailed study, qualitative and quantitative, of these systems would evidently be of great interest for the classification and characterization of disperse systems on the basis of the state of the disperse phases entering into their composition. Transitions from suspensoids to emulsoids and *vice versa* exist also among the colloids proper. Nearly all protein solutions, for example, are emulsoid in character; they are viscous, flocculated only by large quantities of electrolytes, etc. Yet O. Hammarsten,[2] found that a neutral solution of salt-free serum globulin is coagulated by minute quantities of salt (0.1 to 0.3 percent NaCl); and according to W. Erb[3] the same is true of a plant protein, vitellin. According to H. Freundlich and W. Neumann,[4] many dyes show an emulsoid character in aqueous solutions and a suspensoid character in alcoholic solutions. Solutions of these substances in mixtures of the two dispersion media must evidently exhibit transitions between suspensoids and emulsoids similar to those which Friedländer discovered. Systematic investigations in this field would also be of importance for the theory of the colloid state. Finally, we will here point out that one and the same substance may appear either in the suspensoid or in the emulsoid state in one and the same dispersion medium depending only upon the conditions under which it is prepared.

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[1] J. Friedländer, Zeitschr. f. physik. Chem., **38**, 430 (1901).

§12. The Crystalline (Vectorial) Constitution of the Disperse Phase

1. The Concept of Crystallinity.—As is well known, most solid substances as well as a limited number of liquids are characterized by the fact that when their viscosity is sufficiently great their optical, elastic, dielectric, etc., properties are dependent upon the arrangement of their molecules in space. Besides the vectorial nature of these and other properties of such systems, which we usually designate as *crystalline*, these systems assume a definite external shape when their internal friction is sufficiently great. In the most characteristic cases this external shape is made up of a series of plane surfaces. A detailed discussion of the *distribution* of the crystalline state in nature, or of the question of whether so-called amorphous solids are only under-cooled liquids[1] is out of place here. Let it be noted, however, that some investigators like M. L. Frankenheim[2] and P. P. von Weimarn are so convinced of the wide distribution of crystallinity or vectoriality that they have declared the crystalline state "the only internal state of matter." P. P. von Weimarn, especially, believes that the crystalline (vectorial) state is characteristic of all solid, liquid and even gaseous substances, and that generally speaking no amorphous substances exist in nature.[3] But evidently there has been confused here the *possibility* of demonstrating crystalline (vectorial) properties in all manner of substances in every state with the *actual existence* of vectoriality in these as postulated by P. P. von Weimarn. While all gases may be transformed into liquids and most of these into crystalline solids, only a relatively small number of liquids (and of these only certain ones which exhibit special chemical properties such as "molecular chain formation," etc.) are possessed of experimentally demonstrable crystalline properties when in the liquid state; and up to the present time no evidence at all is at hand to indicate the existence of a crystalline structure in gases. From this it follows that the "intensity of the vectorial chaining together of the molecules" (P. P. von Weimarn) is so slight in all gaseous and most liquid systems that it is of no importance. The assumption of vectoriality in these systems is in consequence superfluous, for it leads to no fruitful deductions.

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[1] J. Friedländer, *l.c.*, 432, 433.

[2] O. Hammarsten, Pflüger's Arch., **18**, 38; see also Zeitschr. f. physiol. Chem., 395 (1905).

[3] W. Erb, Zeitschr. f. Biol., **41**, 1 (1901).

[4] H. Freundlich and W. Neumann, Koll.-Zeitschr., **3**, 80 (1908).

It must further be emphasized that the concept of crystallinity or vectoriality is as ambiguous a one as is that of heterogeneity (see the next paragraph). For a system may be vectorial or crystalline in certain of its properties while it is isotropic in others. All solid crystals, for example, are vectorial in *shape*, but crystalline liquids have, generally speaking, only an optical vectoriality. On the other hand, all solid crystals of the regular system, for instance, are *not* vectorial in their refractive indices. Other types of crystals exhibit different degrees of optical vectoriality. A characterization of systems according to their vectoriality is therefore somewhat arbitrary, since it is always necessary to state which of the properties are vectorial. The failure of investigators to consider that different kinds of crystalline systems and different kinds and degrees of vectoriality must be distinguished according to the *kind* and the *number* of the properties of the vectorial state has undoubtedly contributed its share toward confusing the problem of the relations between crystalline and amorphous, solid and liquid states of substances.

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[1] See especially the recent and extensive discussion with references to the literature by C. Doelter, Koll-Zeitschr., **7**, 29, 86 (1910).

[2] P. P. Von Weimarn. See his numerous discussions in Koll.-Zeitschr., **2**, and subsequent volumes, especially **6**, 32 (1910).

[3] The earlier literature is extensively discussed and in part cited verbatim by O. Lehmann, Molekularphysik, **1**, 716, Leipzig, 1888.

2. Direct Proof of Crystallinity in Colloids.—The most frequently applied and simplest practical method of recognizing crystalline properties is the *optical*. As indicated in their definition, it must be impossible to prove by any direct methods such as the microscopic, that colloids possess a crystalline structure. *Ultramicroscopic* methods in place of microscopic can only be of limited use, for they give no direct "image" of the object. A whole series of optical facts have, nevertheless, been accumulated in favor of a crystalline constitution of the disperse phase of metallic sols. These will be discussed in detail when we consider the optical properties of colloid systems. Upon such and similar grounds, investigators like R. Zsigmondy, H. Siedentopf, A. Cotton and H. Mouton have been led to believe in the possibility if not in the probability of the crystalline nature of metallic sols at least.

3. Indirect Proof for the Crystallinity of Colloid Phases.—*The Crystallinity Theory of P. P. von Weimarn.*—Since we have no direct evidence besides the ultramicroscopic upon which to base conclusions regarding the vectorial state of colloid disperse phases we are compelled to resort to indirect means based upon theoretical considerations and extrapolations. Most of these conclusions are based upon the assumption that *particles retain their crystal-*

linity even when their size is progressively changed. Such conclusions were drawn early in the history of colloid-chemistry; and if the "reguline" state of a metal may be considered as crystalline or cryptocrystalline, B. J. Richter (1862) may be regarded as the first to have urged the view that suspensoid phases have a crystalline constitution. By far the most convincing evidence in favor of the view that the disperse phase retains its crystalline state, especially in suspensoids as compared with coarse suspensions (which may be demonstrated to be crystalline by direct microscopic means) has been given by P. P. von Weimarn (*l.c.*). The following seem the more important of the numerous reasons he has advanced in favor of this view.

(*a*) Von Weimarn studied the reactions of formation of a great number of inorganic substances (salts, elements, etc.), directing special attention to the influence of the concentrations of the reacting media. It was found that the shape and the degree of dispersion of the product of the reaction varied greatly and continuously with the concentration. Through experiments on more than two hundred substances he was able to show that *in medium concentrations*[1] *of the reacting substances definite crystals are formed which attain a maximum size at a definite concentration; at concentrations above and below this the crystals become progressively smaller until in extreme concentrations they pass beyond the dimensions of ultramicroscopic visibility.* The systems formed in low concentrations are nothing else than suspensoids identical with those often obtained even before the systematic investigations of P. P. von Weimarn by allowing substances to react with each other in dilute solutions. On the other hand, the systems produced in the *highest* concentrations correspond with the bodies usually described as "jellies" or "glasses." P. P. von Weimarn imagines these, too, to have the composition Liquid + Solid. The continuity with which the size of the crystals decreases with increasing dilution speaks in favor of the view that ultramicroscopic and amicroscopic particles may have a crystalline structure.

(*b*) Another point in favor of the crystalline constitution of suspensoid phases is their power of starting crystallization in *supersaturated* molecular-disperse solutions of themselves. Generally speaking, only such solids have this power which are themselves crystalline. Yet as von Weimarn himself found, highly disperse sols lose this power when their degree of dispersion is sufficiently increased. It is fair to attribute this to the law that the solubility of a substance is dependent upon its specific surface, that is to say, rises greatly with extreme subdivision (see p. 74). Highly dispersed particles would therefore not initiate crystallization in supersaturated molecular-disperse solutions, because the latter are still unsaturated with regard to them. Wilhelm Ostwald's finding[1] that small quantities of salol, made highly disperse by trituration with an indifferent substance, are unable to effect the crystallization of superfused salol, *even though the salol is still demonstrable analytically*, may also be thus interpreted.

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[1] It should be noted that we are dealing with so-called *relative* concentrations, in other words, with amounts of dissolved substances calculated in terms of their maximum solubility. In the case of easily soluble materials the concentration ranges therefore correspond with large ranges of absolute molar or percentage concentrations. On the other hand, with slightly soluble materials, the whole series of different precipitates is included in a small absolute range of concentration.

(*c*) That the particles of sols may *coalesce* to form microcrystalline bodies and even definite crystals after long standing is another fact in favor of the crystallinity of suspensoid phases. Thus P. P. von Weimarn[2] found silver crystals to form in a silver hydrosol after this stood a while. The ultramicroscopic observations of M. Traube-Mengarini,[3] of J. Amann[4] and of L. Pelet and A. Wild[5] who noted the direct formation of crystalline bodies by a simple coalescence of ultramicroscopic particles in colloid lead (lead oxyhydrate), colloid iodine and colloid dyes are even more convincing evidence of the possibility of a "direct colloid crystallization," that is, a direct fusion of ultramicroscopic particles to form definite crystals. One is inclined to believe that only vectorial particles can have the power of growing into definite crystals, just as one believes that only such may produce crystallization in supersaturated solutions. Yet we must point out even here that the crystalline character of these "crystalline elements" has been disputed by a whole series of investigators (see below).

From these and other facts we may conclude that most suspensoids, that is dispersoids having a degree of dispersion of 6.10^5 to 6.10^7 are possessed of a crystalline disperse phase. But serious objections may be raised to the assumption that *all* solid disperse particles are crystalline as P. P. von Weimarn, for example, has advocated. Thus, as mentioned above, the crystallinity of large masses of all solids under *all* circumstances has not been demonstrated experimentally. Even though most substances *may* be obtained in crystalline form, yet under many circumstances the "vectorial chaining together of the molecules" is so slight or so loose that vectorial properties are no longer observable. While it is true that proteins may be obtained in crystalline form, yet the solid precipitates from protein solutions, except as produced under special conditions, exhibit no trace of crystallinity. Under such circumstances it is therefore just as suitable to assume that the intensity of vectorial chaining is zero as to postulate a "latent" crystallinity.

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[1] Wilh. Ostwald, Z. f. physik. Chem., **22**, 289 (1897).

[2] P. P. von Weimarn, Koll.-Zeitschr., **4**, 317 (1908); **5**, 62 (1909).

[3] M. Traube-Mengarini and A. Scala, Koll.-Zeitschr., **6**, 65 (1910).

[4] J. Amann, Koll.-Zeitschr., **6**, 235 (1910).

[5] L. Pelet-Jolivet and A. Wild, Koll.-Zeitschr., **3**, 175 (1908).

4. Dependence of Crystallinity upon Size of Particles.— There remains the possibility that the general assumption upon which all these indirect proofs of the crystalline nature of the colloid disperse phase depend, namely, the *retention* of vectoriality in extremes of dispersion, is not valid for the degrees of dispersion here under discussion. From the behavior of liquids in the process of solidification we are compelled to assume that solids have a positive *surface tension* even though its effects do not become clearly evident because of the great internal friction possessed by solid substances. But, as will be discussed later, the surface energy expressive of this surface tension increases markedly with every increase in the specific surface; in other words, a greater centripetal force acts upon the molecules of highly disperse particles than upon those of coarsely disperse particles. It seems not impossible that such a positive surface tension may produce a deformation in minute crystals, in other words, destroy their structural vectoriality by rounding off their corners and transforming them into spheroidal bodies. As shown by the behavior of liquid crystals, the optical vectoriality, for example, of such a particle need not be destroyed in such a process. It could therefore be possible that the free surface tension of solid particles might attain values in extreme degrees of dispersion sufficient to destroy the vectorial chaining together of the molecules responsible for crystallinity. An investigation of the influence of pressure upon the optical properties of crystalline liquids would be of interest in this connection. Further, it might be possible that a relation exists between compressibility and vectoriality of such a nature that easily compressible substances lose their structural vectoriality at lower degrees of dispersion than less compressible ones, etc.

It is of importance that such an influence of the free surface tension which increases with the specific surface is not only conceivable theoretically but is often demonstrable experimentally. In fact the influence of this factor has been repeatedly observed in that most striking expression of the vectoriality of any system, namely, its crystalline form. As long known from microscopic observation of processes of crystallization, small *spherical* bodies (globulites) are first seen to appear which in no way resemble crystals.[1] It is only after these globulites have attained a certain size that they assume crystalline shape. Crystals with rounded edges are seen to appear, and so on.[2] According to Link, Frankenheim, Vogelsang, Behrens, Quincke, Bütschli, and many others, crystals are often formed by the coalescence of these *microscopically isotropic* globulites, from which there then result "margarites," "honeycombs," etc.[3] It would be of interest to determine whether other changes in the vectoriality of these primary crystals, more particularly changes in their optical properties, also develop as do the structural properties[4] or whether they exist from the first in even the smallest globulites. Such a microscopic investigation might perhaps be extended to ultramicroscopic refraction studies of colloids. If, for example, vectorial differences in the refraction coefficients of many crystals continue to exist when they become extremely small, then the same should be true of the corresponding refraction discs. An investigation of other properties of highly disperse solid particles, such as the thermal and electrical, would also be important.

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[1] See Wilh. Ostwald, Lehrb. d. allg. Chem., 2 Aufl. **1**, 1042.

[2] See the beautiful microphotographs of P. P. von Weimarn in Koll.-Zeitschr., **2** (1908).

[3] Splendid photographs of such honeycomb structures of crystalline materials are found in O. Bütschli, Untersuchungen über Structuren, Leipzig, 1898. See also the numerous, convincing observations of G. Quincke [Ann. d. Physik. (4), **9**, 1 (1902)] as well as the earlier monographs of H. Behrens, Die Kristalliten, Kiel, 1874; H. Vogelsang, Die Kristalliten, edited by F. Zirkel, Bonn, 1875. A partial reprint of the early views may be found in O. Lehmann, Molekularphysik, **1**, 730, Leipzig, 1908. Especial reference should be made to the excellent observations on Asaron of C. Schmidt [Liebig's Ann., **53**, 171 (1845)] who observed a perfectly regular coalescence of four droplets. For a discussion of the vectorial arrangement of coarsely dispersed particles see R. Krulla [Zeitschr. f. physik. Chem., **66**, 126 (1909)]. Wilh. Ostwald [Lehrb. d. allg. Chem., 2, Aufl. **1**, 1040, Leipzig, 1903] also recognizes the possibility of a "discontinuous" development of crystals from particles which were originally spherical. But in the end, the question of the state of these "crystal embryos" is still to be regarded as open (see p. 61, in the text).

[4] It is important to note that we may not apply to all matter a vectoriality observed photographically in the finest precipitates of some solid substances. The degree of effect of positive surface tension upon form depends also upon the internal friction, etc., of the particles and this varies considerably in different cases as evidenced by the so-called "liquid crystals." See in this connection the work of P. P. von Weimarn cited in the footnote on p. 63 as well as the text on p. 61.

Attention should here be redirected to the conclusion reached above, that solid particles become more and more like *liquids* as their degree of dispersion increases; and to the converse of this which P. P. von Weimarn among others has assumed to be the case. It therefore seems possible theoretically that a development of crystals may take place in that the "crystal embryos" are at first *liquid* and only later become solid as they enlarge, either because of a "progressive" coalescence of molecularly-dispersed particles or through a discontinuous union of submolecular phases. That such seems to be the case is evidenced by the investigations of the observers mentioned above. Wilhelm Ostwald (*l.c.*), in discussing the analogous process of crystal formation in molten masses, even says: "The precipitation of the insoluble from liquids seems *always* to occur *primarily*[1] in the form of droplets, that is, in the state of an under-cooled liquid." If the dispersion in such a system were to become fixed at such, or more correctly, at a somewhat earlier moment, a highly disperse system (among which colloid systems would be found) containing a liquid phase would result. In other words, at the beginning of crystallization a *structural* vectoriality would be lacking. Whether an *optical* vectoriality exists at this stage remains to be determined. Finally, it seems safe to assume that the form of development of crystals will also vary with the nature of the crystallizing substance.

It is evident from all this that the question of the maintenance of crystallinity, in other words the question of a *complete* vectoriality of the disperse particles, more particularly of the disperse particles of solids in high degrees of dispersion,[2] cannot yet be settled with entire certainty.

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[1] The italics are mine. This view is also held by G. Quincke (Ann. d. Physik., **9**, **10**, etc.).

[2] P. P. von Weimarn, in a recent paper [Koll.-Zeitschr., **6**, 32 (1910)] holds that an influence of the degree of dispersion upon the form of solid particles only becomes effective if their size is less than 5$\mu\mu$, especially in the case of slightly soluble and difficultly fusible materials. The basis for this is derived from a "purely kinetic viewpoint" dependent upon kinetic views regarding the physics of the various "degrees of orientation" of molecules in the body and in the surface layers of a crystal. I confess that to me this argument is not convincing.

5. Crystallinity of Emulsoids.—Since only a relatively small number of crystalline liquids are known, we may expect to encounter crystalline emulsoid phases but rarely. In fact, while a number of coarse emulsions having a crystalline disperse phase are known[1] not a single example of a crystalline emulsoid is known. This is in part due to the fact that it is rarely possible to make out optically the particles of a disperse phase and thus to investigate their vectorial properties, because of the slight difference of refraction between them and the dispersion medium. It is of course not impossible that future investigators may demonstrate the existence of dispersoids having a crystalline emulsoid phase. In this connection the behavior of crystalline liquids when near their "clarification point" should be borne in mind (see the literature quoted in the accompanying footnotes).

It must further be remembered that all degrees of vectoriality may be demonstrated, particularly in liquids.[2] Not only do we find examples of different degrees of structural, optical, etc., vectoriality among liquid crystals and crystalline liquids, but as shown by O. Lehmann, many different external factors may influence the kind and the degree of vectoriality. Pressure and tension, the "adsorptive power" of solids, magnetic influences, changes in temperature or of the solvent, the presence of other substances, etc., are all of importance. There are liquids which assume vectorial properties only under the influence of powerful external agencies. Thus, A. Cotton and H. Mouton[3] showed that certain organic liquids of high molecular weight become doubly refractive in a strong magnetic field. Similar facts have long been known regarding many typical emulsoids,[4] such as concentrated gelatine solutions (jellies) when under the influence of pressure or tension. As is well known, all the contractile elements of living substance exhibit double refraction.[5] Here we deal with a *temporary* vectoriality which exists only when certain systems are under the influence of transitorily active agencies; or which is produced through the absorption[1] of submicroscopic anisotropic particles. These systems would therefore be classed as possessing the lowest possible grade of vectoriality both with regard to intensity and to number of vectorial properties. From all of which it becomes somewhat arbitrary whether we will follow O. Lehmann[2] and P. P. von Weimarn[3] in describing such systems as possessed of an "artificial vectoriality" and as "liquid-crystalline," or not.

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[1] See the numerous examples in O. Lehmann, Flüssige Kristalle, Leipzig, 1906.

[2] See the lecture of O. Lehmann, Flüssige Kristalle und die Theorien des Lebens, 29, Leipzig, 1906.

[3] A. Cotton and H. Mouton, Compt. Rend., **141**, 317, 349, etc. (1905).

[4] See the numerous examples investigated by G. Quincke, Drude's Annalen d. Physik., **7**, **9**, **10**, **11**, **12**, **13**, **25** (1902 to 1904).

[5] A recent comprehensive presentation of these relations may be found in W. Engelmann, Ber. Berl. Akad. d. Wiss., 694 (1906).

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[1] H. Ambronn, Ber. d. D. Botan. Ges., **6**, 229 (1888); **7**, 111 (1889); Koll.-Zeitschr., **6**, 222 (1910).

[2] O. Lehmann, Verh. d. D. physik. Ges., **10**, 321 (1908); **10**, 406 (1908).

[3] P. P. von Weimarn, Koll.-Zeitschr., **3**, 166 (1908).

CHAPTER III

GENERAL ENERGETICS OF THE DISPERSOIDS

§13. Surface Energies

1. Forms of Energy Characteristic of Dispersoids.—The foregoing pages have dealt with the general and topographical characterization of dispersoid systems, more particularly colloid systems. It is our next problem to discuss the more important forms of energy which play a rôle in these—for like all physical systems, dispersoids exhibit phenomena which are attributable to changes in their thermal, radiant, electrical, chemical, etc., energies. Evidently, physical systems may be classified on the basis of the forms of energy which appear most frequently or most prominently in them. Thus, gases are best characterized by the behavior of their volume energies, while electrical phenomena seem to be especially characteristic of dilute salt solutions. The form of energy most characteristic of the dispersoids is directly deducible from their definition. A *development of much surface* is the fundamental property of dispersoid systems. But the absolute value of this surface is a direct measure of the capacity factor of the so-called *surface energies.* One therefore anticipates that the properties of these and of closely related forms of energy must play an important part in the dispersoids. Especially true is this of all *changes* in the dispersoid state which involve an increase or a decrease in the degree of dispersion; for according to definition every change in the magnitude of the surface must be regarded as the result of free surface energies or of their compensation by other energies. Wilhelm Ostwald pointed out the importance of the surface energies for the theory of colloid phenomena even before their dispersoid character was established on theoretical and experimental grounds.

2. Surface Energy of the First Order.—Surface energy as usually discussed is made up of two components; a capacity factor as measured by the absolute surface, and an intensity factor as measured by *surface tension.* This type of surface energy endeavors to *decrease* the surface of a system if free energy is available. For reasons to be discussed in the succeeding paragraphs we shall call this, *surface energy of the first order* and its intensity factor, *positive surface tension*. Its most important properties are the following.

If surface energy of the first order is freed in any way it is changed into other forms of energy, especially heat, the surface of the system *decreasing* at the same time. Conversely, if heat is introduced into a system capable of developing free surface energy of this order, the surface tension is decreased. Roughly, the decrease in surface tension is proportional to the increase in temperature. If an electric surface is produced, in that two phases having different electric charges which are not permitted to neutralize each other are brought in contact with each other, the surface tension of the phases decreases. Further, the value of the surface tension varies with the chemical character of the phases which are in contact with each other. General laws regarding the relation between magnitude of surface tension and chemical character of the phases have not yet been discovered. The surface tension of a dispersion medium may be lowered or raised by the molecular-disperse or colloid subdivision of a phase in it (for details see page 140). The value of the total surface tension of dispersoids is dependent upon the age of the surface. If the disperse phase lowers the surface tension of the dispersion medium, the value of the tension decreases with time; but if the disperse phase increases the surface tension of the dispersion medium, little or no change is observable. The ultimate value of the surface tension attained after a longer period of time is called the *static* surface tension, in contradistinction to the *dynamic* surface tension observable in freshly produced systems. We shall discuss the reasons for such changes later. Details regarding positive surface tension and the many methods of measuring it with its correlated surface energy of the first order must be sought in text-books of physics and physical chemistry.[1]

3. Surface Energy of the Second Order.—For reasons which we are unable to discuss in detail here we are compelled to recognize the possibility of the existence of another form of surface energy, namely, *surface energy of the second order*. As is well known, two forms of volume energy are characteristic of gases: one which is transformed into other varieties of energy when the volume of the gas *increases*, and a second which is analogous to surface energy of the first order in that it also is converted into other forms of energy when the volume of the gas *decreases*. The intensity factor of this second, less well-known form of volume energy is the so-called "internal pressure." In liquids this attains a value estimated at several thousand atmospheres. Reasoning by analogy we may suspect that a form of surface energy exists which has the tendency to change itself into other forms of energy whenever the surface of a system *increases*. The intensity factor of this type of surface energy might be designated *expansive* or *negative* surface tension. What evidence is there for the actual existence of such a second type and are we familiar with phenomena which may advantageously be explained through its properties?[1]

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[1] A recent and in part exhaustive presentation of the relation of positive surface tension to other physical and chemical factors may be found in H. Freundlich, Kapillarchemie, Leipzig, 1909.

As a matter of fact, certain phenomena are known which can only be explained by assuming the existence of such a surface energy of the second order—an expansive surface tension. These are the increases in surface which occur in strictly *diphasic* systems.

The simplest and clearest expressions of an expansive surface tension are observed when small volumes of liquid, such as droplets or streamlets, are electrified. The phenomena have long been known under the names "electric heart," "electric fountain," etc.[2] The accompanying Fig. 9 taken from O. Lehmann illus-

[1] We frequently encounter in the literature, as in the writings of Maxwell, Mensbrugghe, Wilh. Ostwald, Fuchs, van't Hoff-Donnan, M. Heidenhain, J. Perrin, L. Michaelis, F. Haber, etc., discussions of the possible existence of, and of the effects of the intensity factor of this kind of expansive surface tension. Since the beginning of 1905, partly without the knowledge of the studies of these authors and partly before their papers appeared, I have occupied myself with this concept of surface energy of the second order. Since it led to conclusions which were somewhat surprising and far reaching, I did not dare to publish a monograph entitled "Untersuchungen zur Theorie der Oberflächen- und Volumenenergien" even though the manuscript had been revised for the third time by the summer of 1905. It has been revised and enlarged several times since then and its contents subjected to rigid reëxamination. Because similar views have been frequently expressed, and encouraged by scientific friends, I have at last decided to publish these investigations, even though far from complete, under the title, "Die energetische Atomistik, Untersuchungen zur Theorie der Oberflächen- und Volumenenergien" (Theodor Steinkopff, Verlag, Dresden). Further details regarding the properties of surface energy of the second order and its rôle in dispersoid systems may be found there.

[2] Regarding phenomena of this type see O. Lehmann, Molekularphysik, 1, 824, Leipzig, 1888; H. Freundich, Kapillarchemie 212, 255, 260, Leipzig, 1909. I do not, of course, agree with the theories of the latter which differ fundamentally from mine; see Wo. Ostwald, Koll.-Zeitschr., 7, 142 (1910).

trates the "disruptive" surface increase against turpentine which liquid (molten) sulphur shows when electrified. The left-hand figure shows the effect of a weak, the right-hand that of a strong charge. The liquid sulphur surrounding the rod-shaped electrode first assumes conical shape at the tip of the electrode (this already means increase of surface) and then breaks up into individual droplets. Through strong electrification several such "points of discharge" all showing the same behavior, may be produced. When the electrode is placed in a vertical position, and when the charge is high and the liquid has little viscosity, the phenomenon of the "electric fountain" is produced (see the figure in O. Lehmann's volume). The "electric heart" is the name applied to the changes in form observed when the volume of liquid is weakly electrified (see the point of the electrode in the figure to the left).

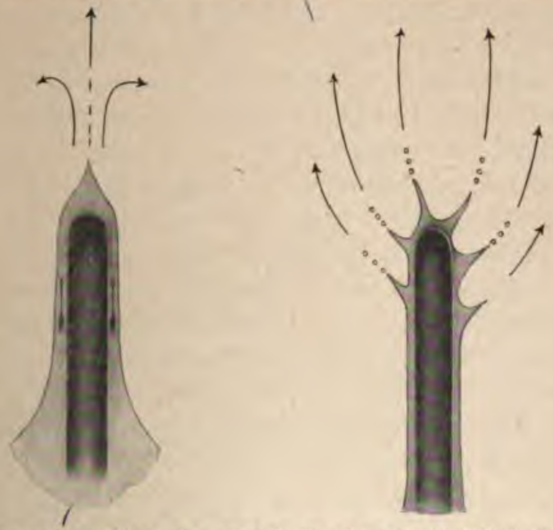

FIG. 9.—Increase in surface, when electrically charged, of melted sulphur against turpentine oil. (After *O. Lehmann*.)

The left-hand figure shows the effect of a weak, the right-hand, the effect of a stronger charge.

Such increases in surface have also been observed when *solid* phases are brought in contact with liquid ones even when no electric energy is available. Of recent investigations of this problem those of M. Traube-Mengarini, A. Scala,[1] and J. Amann[2] deserve special mention. These authors were able to observe microscopically and ultramicroscopically the breaking up of coarsely disperse particles of lead or iodine, in a suitable medium, into smaller but not amicroscopic (molecular-disperse) particles. J. J. von Kossonogow[1] found that electrification promoted these effects. Another striking illustration of an increase in the surface of a "solid" phase is seen in the production of lead sponge from lead plates when a suitable current is passed through them (see pp. 71 and 82).

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[1] M. Traube-Mengarini and A. Scala, Koll.-Zeitschr., **6**, 65 (1910).
[2] J. Amann, Koll.-Zeitschr., **6**, 235 (1910).

In complex dispersoids the phenomena characteristic of an expansive increase in surface remain essentially the same, but they are complicated through the simultaneously occurring changes in concentration and secondary chemical effects. Expansion phenomena are observed when fatty acids come in contact with alkaline solutions; when cholesterin, etc., come in contact with various pure solvents, etc. The so-called "myelin forms" produced under such conditions will be discussed later.

If we bear in mind that all possible transitions exist between coarsely disperse, colloid, and molecular-disperse solutions, we are driven to the ultimate and, perhaps, most important conclusion of all, namely, that the process of molecular or "true" solution is also to be regarded merely as such a spontaneous and extreme increase in surface in a diphasic system.[2]

[1] J. J. Kossonogow, Koll.-Zeitschr., **7**, 129 (1910) where earlier publications are listed.

[2] Even the most modern textbooks of physics state that the only physical requirement for solution resides in a reduction of the positive surface tension to zero. But this really tells us nothing concerning the character of solution, for to prove the *absence* of any energy potential gives no clue to the source of the work necessary for solution. Especial emphasis, therefore, must be laid on the experimental proof of a spontaneous increase in surface in *two*-phase systems. Surface increases due to three positive surface tensions have long been noted in three-phase systems (as in the spreading of oil on water). Regarding the view that solution is a chemical process consisting of the formation of compounds of solvent and solute in indefinite proportions, we need only remark that this assumption, even if correct, does not explain the extraordinary increase in surface which occurs in the process of solution. But this increase in surface is by definition a physical process which like all other physical phenomena depends *among others* upon the chemical properties of both phases but also upon their electrical, thermal, etc., properties, all of which influence the extent of the surface increase. No chemical conception of the process of solution, whatever its nature, is able to explain why a given solid (say tannin) dissolves as a *colloid* in one solvent (water) and as a *molecular dispersoid* in another (alcohol). If we regard the extensive "division" of a dissolved substance as the characteristic of both colloid and molecular-dispersoid solution then every process of solution becomes physical. We can only speak of "chemical" solution (with the exceptions noted above) when free surface energy of the second order is derived *exclusively* or *mainly* from chemical energy. The solution of metals in acids is an example of this sort. For details see the book announced on p. 68.

Regarding the remarkable fact that separate particles are formed immediately in the expansive increase of surface in the case of solid phases (with the exception of lead sponge) while a progressive increase is often observed in liquids, and for further details regarding the conditions for molecular subdivision, see p. 77.

4. The Relation of Surface Energy of the Second Order to Other Forms of Energy.—Since the concept of expansive surface energy is an unfamiliar one, it is necessary to discuss briefly its relation to other physical and chemical factors. Theoretically, many properties of this surface energy of the second order may be predicted, and this on the basis of the fact that the two types of volume energy show in most respects a reciprocal behavior. Thus, positive surface tension decreases as a rule with increasing temperature; conversely, expansive surface tension should increase when the temperature increases. This requirement is satisfied by the general increase in solubility which substances show with rising temperature. Further, the positive surface tension of a system falls if a difference of potential is established at its surface; the negative surface tension should increase under such circumstances. That such is the case was repeatedly demonstrated in the earlier paragraphs of this book. An increase in surface may be effected very generally and often strikingly by different electrical means, as in the production of colloid solutions from non-disperse phases[1] (electric synthesis of the colloids). As already mentioned, but few quantitative relationships have been established between the surface tensions of different substances. A similarly great variation should therefore exist in the values of the expansive surface tension. This requirement is satisfied in our lack of stoichiometrical generalizations regarding both the molecular-disperse and the colloid solubility of substances, etc.

These remarks may suffice to demonstrate the justice of assuming the existence of a surface energy of the second order with the described properties. We shall accordingly make use of this concept in the special parts of this book.

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[1] See Wo. Ostwald, Koll.-Zeitschr., 7, 132 (1910).

§14. Dependence of Surface Energies upon Specific Surface

1. General Considerations.—Relations exist between the surface energies and the *shape* of the phases at the boundaries of contact. These are extremely important. First, as regards surface energy of the first order: As is well known, its most striking effects appear in systems which have *markedly curved* surfaces or which, when possessed of *plane* boundaries enclose a relatively *small* volume. The so-called capillary phenomena in the strict sense of the word illustrate the influence of the markedly curved surface. The effect of the second factor is illustrated in the relation which exists between the height to which a liquid ascends between two glass plates that are in contact with each other along one edge, and the thickness of the layer of the liquid and of the gas above it (see Fig. 10). The thinner the layer, the more definite the capillary phenomena, that is, the higher the ascent of the liquid. The general effect of the influence of the curvature as well as of the thickness of the layer of the liquid upon the magnitude of the surface energy of the first order is expressed in the relation between the surface energy and the *specific surface* of the phases. Thin or markedly curved layers of a liquid are manifestly possessed of a *relatively* greater absolute surface than equivalent volumes of thicker or less markedly curved layers.[1] An *increase* in surface energy in any given volume is therefore

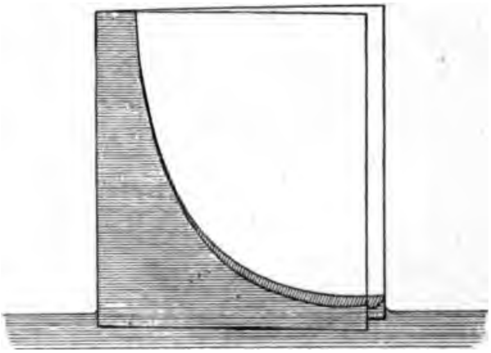

FIG. 10.—Capillary rise and specific surface.

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[1] The same is true of structures in which two dimensions are very small (threads, etc.).

produced whenever more absolute surface is developed or the specific surface is increased.

When we apply this conclusion to typical dispersoids we find that a given volume of the disperse phase, *absolutely* considered, contains more surface energy than the same volume of the same substance in a non-disperse state. But the total amount of surface energy of a *single* particle is also *relatively* increased. Thus, when volume and mass are decreased to $1/1000$ by decimal subdivision of a cube (see Table 1), the surface of one of the resulting cubic particles is only decreased $1/100$. The greater the degree of dispersion, the more surface does the disperse phase "contain." In fact we may say that when the disperse phase is so finely subdivided that the diameter of the individual particles is only twice that of the sphere of action of molecular forces, it "*consists only of surface.*" Evidently the shifting in any system of the relation of the different kinds of energy to each other in favor of those found in surfaces must have a fundamental influence upon the character of these systems.

This growth of the surface energies with increasing subdivision, and their extraordinarily great importance in dispersoids having a high specific surface may be further illustrated as follows:[1] If the "internal energy," that is, the total energy of a system *minus* the surface energy is designated by I, and the surface energy by S, then the total energy of the system equals $I + S$. The quantities of energy comprised under the name "internal energy" (for example, kinetic energy, chemical energy, etc.), are proportional to the volume v, while the surface energies are proportional to the surface s, in other words, $I = iv$ and $S = ts$ when i is the internal energy of the unit of volume and t is its surface tension. The total energy T of a system is therefore $T = iv + ts$. If now we consider the total energy of the unit volume $\frac{T}{v} = T_v$, in other words, if we divide the entire equation by v we obtain $Tv = i + \left(\frac{s}{v} \cdot t\right)$. If $\frac{s}{v}$ is small, that is, if the specific surface of the system is small, the second member is also small and may be neglected. This is the case in most of the physico-chemical reactions hitherto investigated in which interest has chiefly centered upon part i of the total energy. But if v is kept constant and s is increased, as in the subdivision of a given cube for example, the second member may grow tremendously in value. If the subdivision is *very great*, part i, which is proportional to the volume, may disappear altogether in comparison with the value of the second member. Under such circumstances the total energy of the system consists almost entirely of surface energy and all its activities are characterized by the properties of the latter.[1]

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[1] Wilh. Ostwald, Grundr. d. allg. Chem., 4 Aufl., 531, Leipzig, 1909. The above is a somewhat modified presentation of the subject.

2. Surface Energy of the First Order and Specific Surface.—Illustrations of the relations between surface energy of the first order and specific surface were given above. Another example of such a relation is the fact that the height of ascent of a liquid in a capillary tube is inversely proportional to the diameter of the tube; in other words, the product of the height of ascent and the diameter of the tube is a constant. This means that if the diameter of the capillary tube is reduced by half, the height of ascent of the liquid is doubled, and if the former is decreased to one-tenth its value, the magnitude of the latter becomes ten times as great. If we write the surface energy of a cube with an edge 1 cm. long as 1, the surface energy of the same cube *colloidally subdivided* (so as to have cubes with $10\mu\mu$ edges) amounts to 1,000,000 when we assume that the surface tension remains unchanged.

3. Surface Energy of the Second Order and Specific Surface.—Since the surface energy of the second order contains the absolute surface of a system as its capacity factor, we would imagine that its effects should also increase with increase in curvature, decrease in thickness, or increase in degree of dispersion. Is there any experimental evidence for this? It is found in what is called *the influence of the size of the particles of solid substances upon their solubility*. As Wilhelm Ostwald,[2] G. Hulett,[3] and others have shown, substances in a finely dispersed state, as produced by trituration for example, are more soluble than those in a coarsely dispersed state. Hulett found finely triturated mercury oxide to be more than three times as soluble as coarser pieces. The solubility of a highly triturated powder as determined by conductivity measurements amounted to 0.694 millimols (150 mg. per liter). An especially interesting series of experiments of this kind was carried out by Stas in the year 1870 regarding the solubility of the different "precipitates" of silver chloride.[1] Stas found that, depending upon the experimental conditions under which it is obtained, silver chloride assumes the forms: 1. "gelatineux; 2. caséeux, flocconeux; 3. pulvérulent; 4. grenu, écailleux, crystallin fondu;" and that the solubilities of these modifications, the degree of dispersion of which undoubtedly *decreases* in the order given below, was as follows:

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[1] See p. 93 for the interesting conclusions deducible from this discussion.

[2] Wilh. Ostwald, Z. f. physik. Chem., **34**, 496 (1900).

[3] G. Hulett, Z. f. physik. Chem., **37**, 385 (1901); see also Hulett and Allen, Journ. Am. Chem. Soc., **24**, 667 (1902).

1. Flocculent silver chloride 0.0140 gram per liter at 20°.
2. Powdered silver chloride 0.0060 gram per liter at 17°.
3. Granular silver chloride 0.0001 gram per liter at 15°.
4. Granular silver chloride 0.03 gram per liter at 100°.

The solubility of the granular preparation had to be measured at 100° because it is too slight at room temperature to be determined analytically. The solubility of the gelatinous chloride could not be determined because of the difficulty of separating it *in this condition* from the fluid in which it is precipitated and on account of its instability.

A still older observation of this kind was made by Thomas Graham.[2] Graham found that silicic acid jellies of *different concentrations* have different (maximum) molecular solubilities. Thus, only two parts of the silicic acid of a 1 percent jelly formed a molecular-disperse solution in 10,000 parts of water, only one part of a 5 percent jelly, and even less of the more highly concentrated jellies. But silicic acid is a typical emulsion colloid, that is, its degree of dispersion changes with variations in concentration. Concentrated jellies are presumably less disperse than the more dilute and so have a lower molecular solubility.

In harmony with the above-sketched conception of solution as a process of extreme increase in surface produced by a free expansive surface energy, it is evident that such influence must act by effecting an *absolute* increase in surface energy by increasing the specific surface. Such a relationship is rendered plausible by the fact that the "artificial" breaking up of a substance preparatory for solution already represents surface work which is later saved in the process of that further surface increase which we call "*solution.*"

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[1] See K. Drucker, Koll.-Zeitschr., 4, 216, (1909).

[2] Thos. Graham, Journ. Chem. Soc., 1864; see also his collected papers, p. 618.

An interesting observation apparently contradicts this conception of an increase in the surface energy of the second order of a system with its degree of dispersion. According to the concurrent statements of R. Zsigmondy,[1] J. Donau[2] and The Svedberg[3] colloid gold is only slightly amalgamated, if at all, by mercury. But this is really a question of *solution velocity,* not of maximum *solubility.* Besides, this case should not be compared with what was said above, for in the amalgamation of colloid gold by mercury we are dealing with a triphasic rather than a diphasic system; furthermore, an absolutely necessary preliminary condition, namely, *contact* of the two phases is absent. This must first be produced by shaking, etc., and is presumably hindered by the fact that surfaces, especially when markedly curved, are surrounded by liquid films having special properties such as great tenacity, etc., which must be broken before direct contact of the phases and solution may take place (see later).

4. Dependence of Surface Tensions upon Specific Surface.—Besides this influence of the specific surface upon the absolute and relative amounts of the surface energies, there exists another between the latter and the shape of phases encountered when equivalent but differently constituted surfaces are compared. This relation depends upon the circumstance, which has both an experimental and a theoretical basis, that the direct effects of the surface energies extend to a certain depth on both sides of the mathematical surfaces of contact.

In curved surfaces such subsurface effects of the surface energies may weaken or strengthen these, depending upon the convexity or the concavity of the curvature as well as upon the nature of the phase. Thus, in a surface which is convexly curved with regard to one of the phases and which has a positive surface tension, the subsurface effects may strengthen each other in the "convex" phase while they weaken each other in the "concave" phase. Since we must believe that these subsurface effects are produced by the surface energies or that, conversely, the latter are the result of changes in the constitution of one phase produced by contact with another, this mutual weakening or strengthening of the subsurface effects must have a reciprocal influence upon the surface energies, more particularly upon their intensity factors, the surface tensions. If the simultaneous and opposite strengthenings and weakenings of such subsurface effects produced through curvature of the surface do not completely neutralize each other, the surface tension of one and the same surface may assume different values, depending upon its curvature.

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[1] R. Zsigmondy, Liebig's Ann., **301**, 37 (1899).
[2] J. Donau, Monatshefte f. Chem., **26**, 525 (1905).
[3] The Svedberg, Koll.-Zeitschr., **5**, 323 (1909).

Special relationships are encountered when the curvature is so great or when the particles are so small or when a layer of one of the phases is so thin that the layers in which the effects of the surface energies still manifest themselves come very close to each other or into actual contact. As is demonstrable through molecular physics[1] and on thermodynamic grounds,[2] the intensity factors of the surface energies change much under such circumstances. This variableness of the positive surface tension in systems having small dimensions has been demonstrated experimentally by the work of Reynold and Rucker[3] on soap films. Since we have no direct method of measuring *negative* surface tension in systems having small dimensions, experimental demonstration of its variableness has not yet been possible. For its indirect determination molecular dispersoids, or better, ionic dispersoids might be used. Special attention might be directed to the properties of very dilute or extremely ionized solutions of electrolytes and their conductivity or viscosity peculiarities, and these might be correlated with variations in expansive tension.

§15. Reciprocal Effects of the Two Surface Energies

(Theory of Dispersion and Condensation)

1. **General Considerations.**—Ordinarily, only *progressive* variations, that is to say, uninterrupted increases or diminutions in surface are considered when the phenomena of surface tension are

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[1] See Lord Rayleigh, Phil. Mag. (5), **30**, 475 (1890).

[2] W. Gibbs, Thermodynamische Studien, 274, Leipzig, 1892; van der Waals and Kohnstamm, Lehrb. d. Thermodynamik., **1**, 207, Leipzig, 1908.

[3] Reynold and Rucker, Phil. Trans, Roy. Soc., London (2), **171**, 447 (1881); **174**, 645 (1883); **177**, 627 (1886); **184**, 505 (1893). See also P. Drude, Ann. d. Physik. (3), **43**, 158 (1891); Johanott, Phil. Mag. (5), **47**, 501 (1899); (6) **11**, 746 (1906); Schütt, Ann. d. Physik. (4), **13**, 712 (1904), etc.; also A. Pockels, Nature, **43**, 437 (1891); Lord Rayleigh, Phil. Mag. (5), **48**, 331 (1899).

discussed. While the coalescence of liquid droplets when they come in close contact with each other is usually attributed to a surface tension effect, such processes are less satisfactorily explained on such a basis alone than is, for example, the contraction of a soap film. Conditions when droplets are in "close" contact are highly complex in character (see later). An analogous difficulty is encountered when a progressive increase in surface gives way to *droplet formation*. We have before us here the general problem: *Under what conditions does a progressive variation in surface become discontinuous?* It is evident that this question is of special importance in the dynamics of the dispersoids, more particularly in that of the colloids, for these are produced either by increasing the dispersion of slightly disperse or non-disperse systems, or by condensing maximally disperse (for example, molecular) systems.

2. Discontinuous Increase in Surface.—The simplest case of a *progressive* increase in surface is encountered when we observe the form of different sized droplets of a non-wetting liquid such as mercury resting on some solid support like a glass plate (see Fig. 11). The *smaller* the droplet, the greater its relative (specific) surface and the more completely does it retain a spherical form (a). Larger droplets become flattened by their own weight (b), in other words, they *increase their absolute surfaces*. If we attempt to enlarge the volume of the droplet on the plate by adding more liquid to it, the droplet becomes progressively flatter until at a *maximum volume*, different with different liquids, it breaks up into several smaller droplets. Thus, with ordinary materials it is not possible to make a coherent droplet, that is, a continuous layer of more than about 25 cc. of mercury on a glass or porcelain surface.[1] An analogous phenomenon is offered in the well-known fact that *cylindrical* deformation of a given volume of liquid cannot be produced after a certain maximum value has been attained, without having the liquid thread break. We need but call to mind

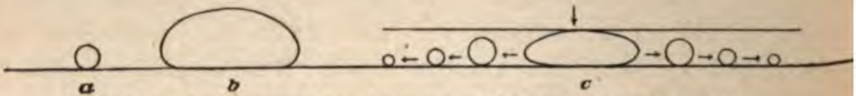

FIG. 11.—Spontaneous changes in shape of drops on a plane surface.

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[1] It is not denied that thinner, continuous layers of mercury might be prepared *by other methods* or by using very pure materials.

the difficulties which must be overcome in the preparation and progressive deformation of fine mercury threads in the making of thermometers. Subdivision of the droplet of mercury may be facilitated by increasing its absolute (and specific) surface "artificially" through the introduction of energy from without as by pressing upon it with a glass plate as shown in Fig. 11, *c*. This increase in surface, which is entirely analogous to that produced through gravity, leads to a dispersion of the drop into droplets which are at first irregular in size, but which approximate the spherical more and more as they become smaller.

Analogous phenomena are observed when a drop of rancid oil is placed upon a *very dilute* alkaline solution in which it changes its shape "spontaneously" and finally emulsifies itself; or when, at a temperature of 40°C., a crystal of cholesterin is introduced into a solution of bile salts.[1] As soon as the *progressive* deformation associated with increase in surface has attained a certain value it becomes discontinuous and the process called "dispersion" begins. This may also be clearly observed in the *electric* dispersion of liquids. We need but recall the facts illustrated in Fig. 9. A weak electric charge produces only a deformation and enlargement of surface, which when a stronger charge is given becomes discontinuous and so gives rise to droplet formation. That a progressive increase of surface may also take place in the "spontaneous" production of colloid and molecular dispersoids is indicated by the appearance in them of "solution figures."[2] One can also easily see that the greater the positive surface tension of a drop of liquid as compared with that of the medium in which it is placed, the more easily will its dispersion be accomplishable. Thus, on the same glass or porcelain plate a drop of water, or better yet a drop of ether, may be spread into a much thinner continuous layer than a drop of mercury. The corresponding surface tensions are: ether, 16.5 (at 20°), water, 70.6 (at 20°), mercury, 436 (at 15°). A somewhat simpler method of demonstrating this relation between the discontinuous enlargement of a surface and its surface tension is to deform liquids by causing them to flow through a capillary tip (see Fig. 12).

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[1] H. Schade, Kolloidchem. Beihefte, **1**, 377 (1910).

[2] See the earlier compilation in O. Lehmann, Molekularphysik., **1**, 481, Leipzig, 1888; where striking illustrations may also be seen.

While ether and water may flow through such a tip in a fine stream (*a*); mercury passes through in the form of droplets (*b*).

It must further be pointed out that, as far as known, all phenomena of dispersion are connected with *movement* of the resulting disperse particles. It is evident that such spatial reärrangements of the disperse particles, in other words, these "dispersion movements" are to be separated theoretically from the process of dispersion itself, in other words, the increase in surface. They are to be considered as phenomena secondary to the transformations of energy which produce dispersion. Regarding the more intimate relationships between the intensity of these movements and the dispersive forces, only suppositions may be made, for no exact investigations of them exist at present.

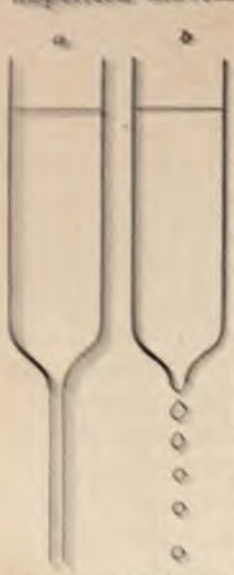

Fig. 12.—Appearance of liquids of slight (*a*) and of great (*b*) surface tension when issuing from a tube.

3. Theory of Dispersion.—All increases in surface are regarded in this volume as expressions of surface energy of the second order. The work necessary for such transformations is made up of the product of the magnitude and of the tension of the surface. It is therefore by definition surface work. From this point of view all increases in surface, whether produced through gravity, through pressure or compression, or by any other means, in other words, all processes of trituration, pulverization, comminution, etc., are only expressions of this surface energy of the second order and differ from each other only in the nature of the sources of the energy employed in bringing about the increase. As previously emphasized, not only mechanical energies but also heat and electrical energies may be transformed into surface energy of the second order, and by this means lead to an increase of surface. Since the increase in surface is always the same, independently of the nature of the energies employed to bring it about, it must remain the characterizing feature of these phenomena.

If we consider one of the simpler effects of surface energy of the second order, as the deformation of a drop of liquid by its own weight, with regard to its possible effect upon the surface energy of the *first* order, we reach the important conclusion that *the decrease in the free surface energy of the second order* when converted into an equivalent of other energies through the increase in surface, *increases the amount of surface energy of the first order in the system,* for the quantity of surface energy of the first order in a system is proportional to the absolute surface when the intensity factor of tension remains constant. If tension is constant—which is certainly the case in the non-disperse and coarsely disperse systems to be first considered—the amount of surface energy of the first order increases with every decrease of the other surface energies. This is true for example when the surface of a liquid drop is progessively increased. But there is no reason for assuming that the increase in surface energy of the first order is always *equivalent* to the decrease of expansive surface energy. Experience shows (see the above-mentioned examples) *that when certain increases in surface are brought about, the increase in surface energy of the first order is greater than the decrease in surface energy of the second order,* for as soon as there exists an excess of contractile surface energy the surface of the given volume becomes discontinuous. The equilibrium between the two energies which is "dynamically" displaced by a slight deformation of the surface is destroyed as soon as the amount of surface energy of the first order produced, more than compensates for the decrease of expansive surface energy. Equilibrium will not be reëstablished until the liberated amount of contractile surface energy has been transformed (into heat for the most part), a change which can be accomplished only by an accompanying diminution in surface. Since the expansile tension prevents a diminution of the volume as a whole this tendency toward diminution can only be satisfied by a *subdivision* of the volume into smaller parts, for then only can both requirements be fulfilled at the same time, on the one hand the *increase* in absolute surface as demanded by the expansile tension, on the other the *decrease* in absolute surface as demanded by the contractile tension. Subdivision is the only possible result; or to put it in another way, the reciprocal effects of these surface energies must lead to subdivision.

Dispersion, or the conversion of a progressive increase in surface into a discontinuous one is characterized energetically by a liberation *of positive surface energy brought about by an excessive development of absolute surface through the effects of expansile surface energy.*[1]

4. Consequences of the Energetic Theory of Dispersion.—If the suggested conception of dispersion is correct, a number of deductions therefrom must be capable of practical support.

It follows from what was said that, neglecting certain transition phenomena, dispersion should set in *suddenly* as soon as a definite amount of deformation has been induced. for discontinuous increase in surface corresponds to an intersection point of two changes in energy. We should expect to encounter especially clear examples of such "critical" points when increases in surface are produced by the transformation of other energies into surface energy of the second order. for then a better control of conditions is possible than in the spontaneous increases in surface. As a matter of fact, such "critical" points have long been recognized, especially in the electric dispersion of liquids and solids. There exists, for example, a so-called "disintegration tension" in all the known electric methods of making colloid solutions,[2] at which the dispersion of the previously non-disperse electrodes suddenly begins.

Further, the critical point should vary with the value of the positive surface tension, in other words, with the value of the free surface energy of the first order of the substance to be dispersed. As a matter of fact, the greater the positive surface tension of the substance to be subdivided, the greater is the amount of surface energy of the second order consumed, in other words, the greater must be the amount of electrical energy, for example, that must be introduced into the system. These deductions are supported by the well-known fact that progressive increases in surface which do not immediately yield disperse systems are observed more commonly in liquids than in solids. As a rule, large quantities of energy are necessary to produce an increase of surface in liquids and then they do not usually yield disperse systems at once. As already mentioned, only certain solids like lead show *progressive* increases in surface. We may explain this interesting difference between solids and liquids by the well-known fact that solid phases possess a greater positive surface tension than liquids as indicated by the progressive increase in surface tension of cooling, molten substances. The transitional behavior of substances like lead is also in harmony with this view.

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[1] A mathematical formulation of the conditions necessary for dispersion on the basis of surface energy will be given in the new book I have announced.

[2] See Wo. Ostwald, Koll.-Zeitschr., 7, 132 (1910).

When we apply this to the question of the dispersive effects of equal quantities of surface energy of the second order upon substances having different positive surface tensions, we find that *the greater the positive surface tension of the substance to be subdivided, the greater the degree of dispersion of the system.* This brings up the question: under what circumstances can we obtain the highest degree of dispersion in one and the same substance? The answer to this is *not* that we must have present the greatest possible amount of free surface energy of the second order. Were this the case then the degree of dispersion of a dispersoid would have to be proportional to its solubility and this is by no means the case. To produce a maximum degree of dispersion a maximum of free surface energy of the *first* order must *also* exist in the system, either to begin with as in solids, or as the *result* of an especially great increase produced *through* an increase in surface. Hence, molecular-disperse systems will be formed when the two surface energies acting between solvent and solute attain the physical maximum. To the important consequences of this characterization of "molecules" in the terms of surface energies for our conceptions of the structure of matter we shall return later (see p. 96).

Let it here be mentioned that F. G. Donnan[1] following a suggestion of J. H. van't Hoff, has constructed a capillary theory of colloid solution in which he also uses the concept of "negative" surface tension. He proceeds from the fact mentioned above that in very thin layers of a liquid the surface tension of a particle is no longer *independent* of the thickness of the layer. On the basis of theoretical considerations which originated with Gauss, he concludes that in layers of such critical thickness the thicker layers tend to spread and become thinner while the thinner layers tend to shrink and become thicker. The resultant constitutes an equilibrium yielding the stable "critical particle." It is evident that this interesting theory[2] differs fundamentally from that outlined above in that the sphere of action of the expansile surface tension is assumed to lie only within the "layers of critical thickness" or the "spheres of molecular activities." According to our view one may observe the effects of expansile surface tension macroscopically, just as one may observe the effects of positive surface tension in coarsely disperse systems, and all independently of the thickness of the layers of particles involved. Moreover, Donnan's view compels him to assume a qualitative difference between colloid and molecular-disperse solutions which is unnecessary in our conception.[1] It is also hard to conceive of the increases in surface until the sphere of molecular activities is reached in Donnan's theory. "It is hard to conceive just what happens. Apparently the solid substance spreads into O (the solvent) in extremely thin layers or in the form of thin branching threads. It should be noted that the solid colloid is not in an *explosive* state, for dispersion takes place only in the thin surface layers so that the process of 'solution' of the colloid need not be a rapid one, etc." (Donnan, *l.c.*, 1901, p. 738). The *progressive, macroscopic, microscopic* and *ultramicroscopic* increases in surface of diphasic systems discussed above show that the energetic theory is easily capable of filling this gap.

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[1] F. G. Donnan, Z. f. physik. Chem., **37**, 735 (1901); **46**, 197 (1903).

[2] It should also be noted that F. G. Donnan in his first paper (1901), outlined a more kinetic theory of colloid solution in that the state of dispersion was regarded as the result of two opposed "molecular streams" occurring in the surface. These processes also take place only "within the molecular spheres of action."

5. Discontinuous Diminutions in Surface.—When one discusses discontinuous *diminutions* in surface one must bear in mind that we deal *not* with diminutions in the surface of the *individual* particles of a dispersoid but with a decrease in the sum of the surfaces of all the particles in the dispersion medium. As a rule, such decreases in total surface are produced by *approximation* or *coalescence* of the individual *smaller* particles into larger ones. It is important to note that such decreases need not take place only through *condensation* (agglutination, agglomeration, coalescence, etc.). Slight decreases in surface may be accomplished when for any reason elongated or flattened particles become more spherical. Tendencies toward such progressive reductions in surface are encountered when dispersoids are cooled. So far as known, the positive surface tension between two (homogeneous) phases always increases with decrease in temperature. Under such conditions irregularly shaped particles would therefore tend to become more spherical with fall in temperature. Yet the amounts of such internal diminutions in surface would at all times be small.

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[1] See p. 134 concerning the "saturation point" of colloids postulated by Donnan.

The "condensation" type of diminution in surface is important in determining the properties of disperse, more particularly of colloid systems. In coarsely disperse systems it shows itself in the coalescence of emulsified particles, in the formation of threads and flakes from microscopic precipitates, etc. It may be observed ultramicroscopically in colloid systems as a union of ultramicrons to form crystalline or non-crystalline particles. In molecular-disperse systems the process of "crystallization" is encountered, attained at times only after passing through an intermediate stage (see above). Generally speaking, such condensations are *produced* by the same means which accomplish their *dispersion*, only different intensities, concentrations, etc., have to be used. Thus, while electric energy has a dispersive effect, removal of the charge leads to condensation, especially in colloids. On the other hand, under proper circumstances and with certain charges, *condensing* effects may be accomplished electrically, as in the coalescence of electrified droplets.[1] Changes in temperature within certain limits and additions of foreign, especially ionized, substances have similar effects. Mechanical treatment, like sudden one-sided pressure, may also bring about condensation, especially in coarsely disperse systems.

When we study a simple case of condensation, as the coalescence of two liquid droplets, we find it hard to follow the *transition* changes from the original state to the final. Coalescence usually takes place very rapidly so that the two droplets *suddenly* become one, though it may still be possible to observe the contractile effects of the positive surface tension in the movements of the surface. To study such processes of condensation in detail it is best to use drops of viscid material[2] which consume more time in the process. The intermediate phenomena, which we shall find of special theoretical importance, may then be studied to better advantage.

Intimate contact of the droplets of a system with each other seems to be an absolute pre-requisite for coalescence (as well as for the union or clumping of solid particles). The droplets must be brought so close together that *their surfaces have at least one "point" in common.* To put it another way, condensation of two particles can occur only when their surfaces are *continuous,* even though such surface continuity be limited to a single point. It should be noted that we mean a "physical" and not a "mathematical" point, in other words, a structure at present unmeasurable but nevertheless of *finite* dimensions. Such a point, greatly "magnified" and fixed at the beginning of its development shows itself as a cylindrical or doubly coniform neck, as illustrated schematically in Fig. 13 taken from L. Michaelis. This connecting piece broadens during coalescence until complete condensation is attained.

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[1] See Lord Rayleigh, Proc. Roy. Soc., London, **28**, 406 (1879); **34**, 130 (1882).

[2] See J. Loeb, Koll.-Zeitschr., **3**, 113 (1908); L. Michaelis, *ibid.*, **4**, 55 (1909).

Sometimes (especially in viscid and in solid disperse particles) another type of contact may be encountered which does not correspond with the description just given. Here the particles also approach each other very closely but do not come in direct contact. In other words, while fixed to each other they are nevertheless still separated by a very thin layer of the dispersion medium. The adhesion of iron filings to magnets or of powders to hot objects, etc., are macroscopic illustrations of such contacts. The precipitation of coarse suspensions (of kaolin, quartz, etc.) illustrates the same phenomenon in a disperse system. It is probably characteristic of such "flakes" that the individual particles in them are separated from each other by a distance *less* than the diameter of the surface tension films. Figure 14 represents the matter diagrammatically. Even though the individual particles in this type of contact are not in themselves *continuous, the liquid membranes of their surfaces are* (see Fig. 14). Because of this difference it seems well to distinguish between the two and to designate the former as condensation while the latter is better called "aggregation." Evidently aggregation may often lead to condensation, and conversely aggregation may be assumed to constitute a precursor of condensation.

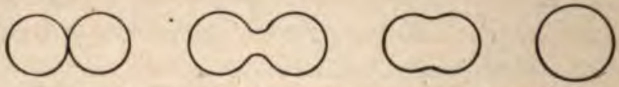

FIG. 13.—Diagram of coalescence of two fluid particles. (According to *L. Michaelis.*)

As is well known, special means have to be employed to bring about such intimate contact or continuity of surfaces. One of the chief factors which tends to prevent this is the fact that the dispersion medium (gas or liquid) exists at the phase surfaces in a denser state, has in other words a so-called surface viscosity. These envelopes act like the vapor envelopes about the drops of liquid formed when water is poured on a hot surface; they cause a "repulsion" of the particles when they meet accidentally and so tend to prevent their coalescence. These phenomena are closely related to the processes of "wetting" touched upon above. Stress was laid upon the importance of these envelopes in phenomena of condensation early in the history of colloid-chemistry. Thus, J. M. van Bemmelen wrote in 1888: "*I think it possible that the formation of the flakes which are precipitated in a liquid is dependent upon a change in the surface tension of the liquid membranes surrounding the colloid particles, of such type that these membranes between the particles are torn at some point, thus permitting the particles to form aggregates.*"[1]

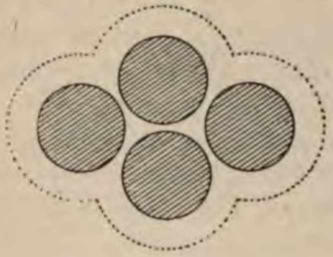

FIG. 14.—Diagram illustrating condensation.

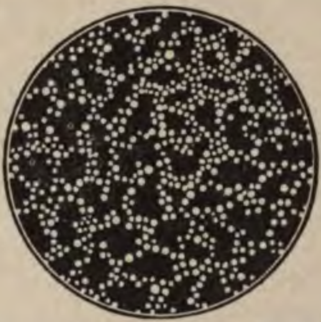

FIG. 15.—Appearance preceding coagulation in a concentrated gold solution. (According to *H. Siedentopf.*)

The condensation of disperse particles is connected with phenomena of movement just as is their dispersion. These "condensation movements" consist of a mutual approach of the particles and are also a necessary preliminary for their contact and coalescence. In fact these movements *precede* contact. The first demonstrable changes in a process of condensation are therefore *kinetic* in character. This fact is of importance for the theory of condensation.

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[1] J. M. van Bemmelen, "Die Absorption" Gesammelte Abhandl., 22, Dresden, 1910. The passage quoted is printed in italics in the original also.

The appearance of such condensation movements is not a mere theoretical assumption but a necessary conclusion derived from the experimentally observed behavior of disperse systems before and after processes of condensation have occurred in them. Such condensation movements have actually been observed both microscopically and ultramicroscopically as illustrated in the accompanying Fig. 15 taken from Siedentopf.[1]

6. Theory of Condensation.—If we attempt to analyze the processes of condensation from an energetic standpoint as was done with the phenomena of dispersion, we discover that the former are more complex. In dispersion the phenomena of surface energy are the primary ones, while processes of movement, the formation of liquid films, etc., are secondary. But in the processes of condensation these different secondary phenomena must take place in reverse order before the surface phenomena proper come into play. Such considerations harmonize with the fact that phenomena of condensation and the means of initiating them are manifold in character as will appear later when we discuss the phenomena of coagulation. The theory of condensation therefore divides itself into two parts, first, to put it briefly, the means by which "intimate contact" of the particles is brought about, and second, the analysis of the processes taking place after contact has been established. Since a discussion of the different means by which the intimate contact of the particles is assured belongs to the field of special dispersoid and colloid-chemistry, this must be postponed.

Subject to general discussion here are the changes which begin when the particles of a dispersoid begin to aggregate. This process is characterized by the formation of a common liquid film about the particles. Since this surface film grows *smaller* in the process of aggregation,[2] the whole seems to be produced through the action of surface energy of the first order. It is also clear that with any increase in the contractile surface energy the liquid film tends to push the particles closer and closer together until they come in actual contact. When we deal with liquids, coalescence of the particles then occurs as described above. In the case of solids (provided we are dealing with actual phenomena of condensation such as crystal formation) there is a coalescence of at least the solid surface layers. The action of the positive surface energy in the latter case may be imagined as shown in Fig. 16. *There results in all instances a decrease of the total surface separating the disperse phase from the dispersion medium. The process of condensation is therefore to be regarded as the consequence of a transformation of surface energy of the first order.* The greater the condensation, that is, the smaller the resulting absolute surface separating disperse phase from dispersion medium, the greater the amount of surface energy of the first order that has been transformed.

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[1] See H. Siedentopf, Verh. d. Dtsch. Physik. Ges., 1910, 25.

[2] See in this connection the quotation from J. M. van Bemmelen, on p. 87.

Processes of condensation do not always yield coarsely disperse or non-disperse systems but may stop when very different degrees of dispersion have been attained depending upon the concentration of the reaction mixture, as shown in the formation of precipitates in chemical reactions (P. P. von Weimarn). This variety in *degree of condensation* is analogous to the above-discussed variety in degree of *dispersion* under different experimental conditions, and must therefore have an analogous energetic significance. *The degree of dispersion in a condensing system depends upon the amount of expansive surface energy present in it.* The smaller the surface becomes by condensation, the greater must become the tendency of the expansive surface energy to counteract the diminution of surface. The system becomes stable when an *intermediate* degree of dispersion has been attained, in other words, when the surface energy of the second order balances the surface energy of the first order which is producing the condensation. The influence of the introduction of other forms of energy upon the degree of condensation is analogous to the influence of these as discussed for dispersion on p. 82.

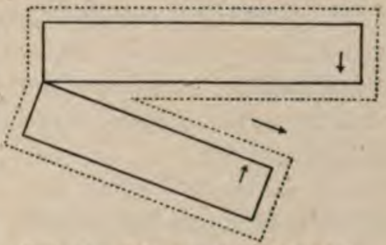

FIG. 16.—Diagram illustrating the theory of condensation.

A relation between condensation in colloids and surface energies was first pointed out by G. Bredig[1] in explaining a special form of coagulation. At an even earlier date P. Curie[1] pointed out the rôle of surface energy of the first order in bringing about condensation in molecular-disperse systems in processes of crystallization. It is remarkable that the important suggestions of this investigator have received but slight (or one-sided) development since they were first expressed. P. P. von Weimarn (whose numerous papers appear in the Kolloid Zeitschrift and in the Kolloid-Chemische Beihefte) has also developed theories of condensation and dispersion which he believes to be so universally applicable that he would explain through them all known processes of condensation and dispersion. A detailed account of his views cannot be given here. It should, however, be emphasized that no theoretical conception of such processes can be formulated comparable in universality with the energetic one which must by definition always remain the broadest form in which natural phenomena may be described. P. P. von Weimarn in his theories of condensation and dispersion often makes use of moleculo-kinetic conceptions, in other words, he employs special expedients in the elaboration of his views.[2]

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[1] G. Bredig, Anorg. Fermente, 15, Leipzig, 1901.

§16. Influence of the Specific Surface upon the Relations between Surface Energies and Other Forms of Energy

1. Specific Surface and Volume Energy; Capillary Pressure.—The relation between surface energies and *volume* energies plays an important rôle in the phenomena observed in dispersoids. If the surface energies are not confined to a plane surface, in other words, if we deal with structures having a spatially defined surface or one which is curved, than the two surface tensions exert pressure. To put it more correctly, the surface energies in such bodies, more particularly in curved surfaces, readily change into volume energies when opportunity for such change offers. Thus, in the positive surface tension of a markedly curved system the centripetally directed capillary pressure may bring about a change in the pressure. If we assume the particle to be spherical, the value of this pressure is *inversely proportional to the radius* and directly proportional to the surface tension. Analogous phenomena are encountered when the curved surfaces have a negative surface tension. As indicated above[1] these relations between surface and volume energies may be demonstrated experimentally and are of course of great importance in dispersoids. It will be shown later that an *increase* in density due to positive capillary pressure may be demonstrated experimentally.

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[1] P. Curie, Bull. Soc. Min., **8**, 145 (1885).

[2] Objections may be raised against certain details of the argument of this author. According to his theory, electrical methods of pulverization are explainable only as condensation processes, which is obviously wrong in view of the dispersing effects of electrical energy described and illustrated on p. 69. Furthermore, he formulates the basic idea of his theory thus: "When, for any reason, the intensity of the dissolving forces increases on the surface of the dispersed particles, but does not exceed that value at which the velocity of crystallization or of solution becomes considerable, then the dispersed particles are peptized (dispersed) by the dispersion medium." [Kolloidchem. Beih., **1**, 398 (1910)]. I can see in this only a "translation," and not an analysis of the process of dispersion, for the assumption of "dissolving forces" and of a relation of these to other processes constitutes the *problem* of dispersion but does not solve it. These objections, however, are not valid if von Weimarn's theories are limited to condensation and dispersion phenomena produced by *chemical* means. As will become evident later, the theories of P. P. von Weimarn agree throughout with the phenomena observed in this particular field.

2. Specific Surface and Changes of State.—The surface energies which dominate the behavior of disperse systems are also much influenced by temperature (and corresponding herewith, by pressure). Thus the vapor pressure of small droplets or particles is found to be greater, at a given temperature, than that of the same substance in larger masses. Smaller drops therefore tend to evaporate more easily than larger ones, wherefore, in a closed system these recondense[2] upon the larger ones. A lowering of the melting point of solid bodies occurs when their specific surface is increased, just as does a decrease in the evaporation temperature with increasing specific surface. Thus P. Pawlow[3] found dusts of salol, antipyrin, etc., to melt at a temperature some 7° lower than larger particles. He calculates that in the case of salol, a depression of the melting point of 2.8° about corresponds to a hundredfold increase in specific surface. A far-reaching influence of the specific surface or curvature is indicated also in the phenomena of solidification or freezing of homogeneous systems. According to Müller-Thurgau,[4] filter paper, moistened with distilled water, freezes at −0.1°, while a clay sphere, moistened with water, freezes, according to Bachmetjew,[5] at −0.7°. These figures are not simply so called under-cooled values for water, but indicate freezing temperatures after such under-cooling is eliminated.

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[1] Wilh. Ostwald, Grundr. d. allg. Chem., 4 Aufl., Leipzig, 533, 1909.

[2] Wilh. Ostwald, Lehrb. d. allgem. Chemie, 2 Aufl. II, **2,** 362; Z. f. physik.Chem., **22,** 289 (1897).

[3] P. Pawlow, Z. f. physik. Chem., **65,** 1, 545 (1909); **74,** 562 (1910); Koll.-Zeitschr., **6,** 37 (1910); **7,** 265 (1910); P. P. von Weimarn, *ibid.*, **6,** 32 (1910); **7,** 205 (1910).

[4] Müller-Thurgau, Landwirtschaftl. Jahrb., **9,** 176 (1880).

[5] Bachmetjew, Z. f. wissensch. Zoologie, **66,** 584 (1899).

In these processes of evaporation, of melting and freezing, a number of energies change. Positive and negative changes in volume and density take place, solid bodies acquire, on melting, free surface energies of the first order, the optical properties change etc. For these reasons it is, as yet, not possible to show the relations which exist between *single* energy changes and the simultaneously appearing changes in the surface energies, the effect of which increases with increasing specific surface.

3. Specific Surface and Electrical Energy.—The relations between electrical energy and surface energies must also change when macro-heterogeneous are compared with disperse systems. Th. Des Coudres[1] showed that in harmony with our theory, a difference of potential between curved and flat surfaces of mercury may not only be proved experimentally but its value be approximately calculated. Of the influence of an electrical potential opposing the positive surface tension, O. Lodge[2] states that in a drop this influence *increases inversely as the fourth power of the diameter of the drop*. In this connection should also be mentioned the important study of H. von Steinwehr[3] who found that finely ground calomel, as used in the preparation of normal electrodes, shows a greater difference of potential toward its saturated solution than does the same substance when less highly dispersed. Further relations between the value of the specific surface of electrodes and electrochemical phenomena may be found in the paper of G. Bredig and J. Teletow.[4]

We would expect, on general principles, that the relations between surface energies and electrical energy would play an especially important part in the case of dispersoids. The majority of electrical phenomena take place on the surface since electrical energy, in contrast to heat, for example, tends to reside on the surface of a homogeneous body. The electrical capacity of a hollow metal condenser is therefore about as great as that of a correspondingly large solid body. Electrical energy will therefore often enter easily into reciprocal action with the surface energies. The great importance of these electrical phenomena in colloid systems will become apparent later.

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[1] Th. Des Coudres, Wiedem. Ann. d. Physik., **46**, 292 (1892).

[2] Wm. C. McC. Lewis, Koll.-Zeitschr., **5**, 91 (1909); also E. Hatschek, *ibid.*, **7**, 158 (1910).

[3] H. von Steinwehr, Z. f. Instrumentenkunde, **25**, 205 (1906).

[4] G. Bredig and J. Teletow, Z. f. Elektroch., **12**, 589 (1906).

4. Specific Surface and Chemical Energy.—Since colloids belong to the heterogeneous systems, the general law of chemical kinetics governing such systems, may be applied to them. This states that *the amount of chemical change in the unit of time is proportional to the absolute surface* (Wenzel).[1] This leads one to suspect, because of the extraordinarily large absolute surface in colloids, that many reactions will occur more rapidly in them than in coarse heterogeneous systems. Such is, in fact, true. M. Raffo and A. Pieroni[2] found that colloid sulphur behaved toward silver salts like an energetic reducing agent; while non-colloid sulphur, even though finely divided and obtained by precipitation of a polysulphide, would not form silver sulphide in the cold. Even after prolonged boiling this occurred only partially. The reactions of precipitated metallic silver vary according to the size of its particles. The coarsely dispersed "gray" silver, obtained by reduction with oxalates, is less sensitive to mercuric chloride than is the highly dispersed "black" silver, precipitated by sulphites, etc. (R. Liesegang, Lüppo-Cramer).[3] Analogous relations exist in the decomposition of hydrogen peroxide by platinum. While smooth platinum foil decomposes this compound slowly, a "platinized" foil (one covered with finely divided metallic platinum) does it more rapidly. When colloid platinum is used, the effect is still observable, if there is but 1 gram-atom of platinum in 70 million liters of the reaction mixture (or 1 gram-atom of colloid palladium in 26 million liters: or 1 gram-atom of colloid gold in one million liters).[4]

Still greater surface effects are naturally to be expected when, as in the last example, we deal with phases having different specific surfaces, that is, having different surface concentrations in space. From the existence of capillary pressure and from the changes in density which result from this pressure we would expect an influence upon the velocity of chemical reactions, for the speed of a chemical reaction is primarily dependent on the density of concentration of the reacting components. Therefore, we would expect that the phenomenon of *catalysis* would be especially marked in colloid systems. The distinguishing characteristic of a catalyzer resides in the enormous change which it is capable of bringing about in the velocity of a chemical reaction. Thanks to the brilliant investigations of G. Bredig,[1] his students and others, it has been shown that many catalytic effects may be brought about by highly dispersed surfaces of all kinds, and that the especially important catalytic reactions of the organic *ferments* may be closely imitated by various *inorganic* materials in the colloid state, such as the colloid metals. We need in illustration but to recall the catalytic effects on gases of a trace of platinum sponge or platinum black as compared with the effects of a piece of smooth platinum foil. The great part played here by the *specific* surface, that is, the volume concentration of the surface, is also apparent.

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[1] See Wilh. Ostwald, Grundr. d. allg. Chemie, 4 Aufl., 328, Leipzig, 1909.

[2] M. Raffo and A. Pieroni, Koll.-Zeitschr., **7**, 158 (1910).

[3] Lüppo-Cramer, Koll.-Zeitschr., **3**, 35 (1908).

[4] G. Bredig, Bioch. Zeitschr., **6**, 315 (1907); G. Bredig and J. Teletow, Z. f. Elektroch., **12**, 581 (1906); J. Teletow (abstract), Chem. Centr., **1**, 793 (1908).

Closely connected with density changes of great surfaces are the so-called *adsorption* phenomena, which we shall consider in detail later. With these are also connected changes of a chemical nature and reaction accelerations. But since they cannot be discussed to advantage without a previous discussion of adsorption itself, we must postpone the whole matter. Even now, however, we may point out that theoretically the amount of a reaction product ultimately obtained, in other words, the equilibrium point in a chemical reaction, may be shifted under the influence of great spatial concentrations of the surface energies, as obtain in dispersoids, for example.[1] If a chemical reaction occurs in the zone of contact between two phases, in which, for example, a positive surface tension is present, either of two things may happen. The surface tension may be either raised or lowered by the chemical change occurring in the two phases. In the first instance, the "chemical resistance," that is, the speed of the opposing reaction, would be decreased through the consumption of energy necessary for the increase in the surface tension; in the second, wherein the surface tension diminishes, an acceleration of the reaction would occur, for the free surface energy produced would now tend to change into chemical energy. Besides the increase in rate, there would also be an increase in the product of the reaction, since the amount of chemical energy available for its formation is increased by the amount resulting from the transformation of surface energy into chemical energy. A great specific surface will therefore be able to shift the equilibrium point of a chemical reaction just as does a rise in temperature. Ostwald[2] has given a practical illustration of this. If the the solution of a salt of a fatty acid is brought in contact with a large surface, the fatty acid set free by hydrolysis tends to collect in the surface, that is, it concentrates itself there more than does the base. The hydrolytic equilibrium of the remaining solution is thereby disturbed, and to reëstablish it, more of the salt must hydrolyze. Other phenomena of this class, especially as observed in colloid systems, will be discussed later.

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[1] G. Bredig, Anorganische Fermente., Leipzig, 1901; further, the recent review of the author in Bioch. Zeitschr., **6,** 283 (1907); here may also be found many references to the literature. The following according to Bredig, are the best connected presentations of the field. Bodlaender, Über langsame Verbrennung, Stuttgart, 1899. W. Ostwald, Grundr. d. allgem. Chem., 1909; Leitlinien der Chemie, 1906; Über Katalyse, Leipzig, 1902; Natur-philosophie, 1902. Sv. Arrhenius, Immunochemie, Leipzig, 1907; Theorien der Chemie, Leipzig, 1906. W. Nernst, Theoret. Chemie, 1909. W. Herz, Lehre von der Reaktionsbeschleunigung., Stuttgart, 1906. R. Hoeber, Physikalische Chemie der Zelle u. d. Gewebe, Leipzig, 1906. E. Cohen, Physical Chemistry for Physicians and Biologists, Trans. by M. H. Fischer, New York, 1903; H. J. Hamburger, Osmotischer Druck u. Ionenlehre i. d. mediz. Wiss., Wiesbaden, 1904. G. Bredig, Elemente der chemischen Kinetik, in Spiro u. Ashers Ergeb. d. Physiol., 1902. Schade, Bedeutung der Katalyse in der Medizin, Kiel, 1907. M. Bodenstein, Chem.-Zeitg., **26,** 1075, 1902. J. W. Mellor, Chemical Statics and Dynamics, London, 1904; H. Freundlich, Kapillarchemie, Leipzig, 1909. Comprehensive presentations by Bredig appear in Oppenheimer's Handb. d. Bioch. as well as in Bredig's Handb. d. angewandt. physik. Chemie.

Finally, it should be noted that several exceptions have been observed to the general rule that substances with large specific surfaces react more rapidly than coarsely dispersed ones. McIntosh[3] states that colloid silver dissolves very slowly in acids. Its solution can be greatly accelerated by the addition of small amounts of permanganate. Occasionally in the literature of colloid-chemistry, we encounter the statement that colloid solutions react "sluggishly." In the light of our discussion, this statement is not correct when comparison is made between colloidally and coarsely dispersed systems. But when comparison is made with the reactivity of molecular and ionic dispersoids, it is. It has been proved with any two substances composing a dispersoid that the reactivity decreases progressively with decreasing degree of dispersion. In molecular and ionic dispersoids in which it might be said that the disperse particles consist "almost entirely of surface," one would therefore expect an enormous development of surface energies. In this connection, one is, as a matter of fact, reminded of the old chemical saying, "Corpora non agunt nisi soluta." But the part played by the chemical energy resulting from the conversion of surface energies during chemical reactions in disperse systems, must also decrease with increasing degree of dispersion. When we come to deal with maximum degrees of dispersion, in other words, with "indivisible" particles such as molecules, atoms or even electrons, one might develop a conception according to which chemical reactions, that is, the union and separation of molecules or atoms, etc., represent merely the results of decreases in the surfaces of the particles involved. The dynamics of molecules and atoms and especially the effects of chemical energy can in this sense come to be viewed as mere manifestations of the surface energies of maximally dispersed particles. The **discontinuity of matter** in which we have always believed and which has been proved in various ways then becomes synonymous with the existence of an immensely great absolute, as well as specific surface; and all changes in this discontinuity become connected with changes in the amount of the surface, or of the degree of discontinuity of the substance, in other words, with changes in the capacity factors as well as the spatial concentrations of the surface energies.[1]

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[1] J. J. Thomson, Applications of Dynamics to Physics and Chemistry, 203, 234, London (1888); see also the extensive discussion of this question but one not free from objection, by T. B. Robertson, Koll.-Zeitschr., **3**, 49 (1908). That the osmotic equilibrium between two molecular dispersoids, and that the distribution of a molecularly dispersed substance between two phases depends on the specific surface of the phases has been proved theoretically by F. Kaufler, Zeitschr. f. physik. Chem., **43**, 686 (1908).

[2] Wilh. Ostwald, Z. f. physik. Chem., **62**, 512 (1908).

[3] McIntosh, Amer. Journ. Physic. Chem., **6**, 17 (1902).

5. Specific Surface and Radiant Energy.—The connection between specific surface and another type of energy, namely, radiant energy, is closely related to the chemical phenomena discussed in the previous division. Stas[1] found that the *photochemical sensitiveness* of silver chloride precipitates increased with their degree of dispersion. Corresponding to the series given on p. 75, the sensitiveness to light increased from the granular, through the powdered, up to the flocculent or cheesy. Interestingly enough, Stas emphasized that it is the latter type and not the "gelatinous" state of silver chloride which is most sensitive to light. Were we to assume, as does P. P. von Weimarn, that the gelatinous is only a continuation of the other varieties of precipitates, in the sense that the precipitate in the gelatinous form represents merely a still finer division of the particles, but is otherwise of the same general character, is crystalline, for example, then the behavior observed by Stas would constitute a contradiction of Wenzel's law. But not only the improbability of such an exception but many other reasons indicate that in "gelatinous" silver chloride we are dealing with a system fundamentally different from that characterizing the other solid precipitates. It is an *emulsoid* in contrast to the others which are *suspensoids*.

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[1] The history of science teaches that we have always held to the theory of the discontinuity of matter, but that different kinds of energy were in turn made responsible for or associated with the elementary changes in the discontinuity. Distance energy (attracting and repelling forces) kinetic energy, and more recently, electrical energy have in turn been associated with the discontinuity. It is of interest to point out that this electrical theory of the structure of matter is closely allied with the concept that the surface energies are the forces responsible for the elementary changes in discontinuity, for, as pointed out above, electrical phenomena occur chiefly on surfaces. It seems, therefore, but a further step in the same direction, if we add surface tension and surface energies to the "forces" already considered, since both of them are as widely distributed and important as the discontinuity of matter itself.

These relations between photochemical sensitiveness and size of granules have often been observed since Stas's work and have attained great importance in the practice of photography and in the preparation of photographic films.[2]

A more interesting, and perhaps more important discovery is the unusual one of E. Wedekind and H. Baumhauer[3] (together with Gockel) that the emanations of radio-active substances may be *much* increased if they are highly dispersed, as by being converted into colloid form. These authors succeeded in preparing radio-active thorium in colloid form. A comparison of the radio-activity of this thoriumsol with that of the metallic (coarsely dispersed) element, measured by the volt decrease per hour, showed the surprising fact that the radio-activity of a sol containing only 0.0235 gram was equal to that of a coarsely dispersed suspension containing 0.111 gram. In other words, *the radio-activity*

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[1] Stas, see K. Drucker, Koll.-Zeitschr., **4**, 216 (1909).

[2] See Lüppo-Cramer, Kolloidchemie u Photographie (Dresden 1908) as well as the numerous papers of this author in the Kolloid Zeitschrift.

[3] E. Wedekind and H. Baumhauer, Koll.-Zeitschr., **5**, 192 (1909).

of the sol was 4.8 *times as great as that of the coarsely dispersed element.*

The extraordinary significance of this discovery[1] lies in the fact it has not as yet proved possible to influence markedly the emanation from a radio-active substance by any other means[2] as by raising the temperature,[3] evacuation, electrolysis, etc. A more striking demonstration of the great effect of the surface energies which come into play with increase in dispersion could scarcely be found than this singular effect of degree of dispersion upon the radio-active disintegration of the elements. Furthermore, this fact seems to indicate that the surface energies will come to play not only an important, but, in comparison with the other kinds of energy, perhaps a dominant part in a general theory of matter.[4]

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[1] It was not recognized by the authors themselves.

[2] See the Textbooks on Radio-activity.

[3] Recently an insignificant influence of temperature has been observed (Engler, etc.).

[4] It would be a feat in colloid chemistry to carry out analogous experiments with colloid radium salts. Since colloid, especially suspensoid systems exhibit their characteristic properties with the most minute amounts of disperse phase, only small amounts of radium salts would be necessary. One might first test out their preparation by using the physico-chemically similar barium salts, and after having discovered a suitable "micro-chemical" method apply it to radium. Gelatinous radium salts could perhaps be prepared by methods analogous to those used by C. Neuberg and his students (Koll.-Zeitschr., **2**, 321, 354) on barium salts in alcoholic solvents.

CHAPTER IV

DISTRIBUTION OF THE COLLOID STATE AND THE CONCEPT OF COLLOID CHEMISTRY

§17. The Fundamental Independence of the Colloid State of the Chemical Nature of the Phases

1. Statistical and Experimental Development of the Idea of the Universality of the Colloid State.—In the forthcoming historical portion of this work it will be shown that the number of known colloid systems has steadily increased as colloid chemistry has developed. In Graham's time (1861) and even later, colloidality was generally held to be characteristic of certain substances, but with the discovery of general *methods* of preparing colloid systems, it soon became clear that this was too narrow a view. At the present time, we may say that practically all solid substances have been, or can be prepared in colloid form by some method or other. P. P. von Weimarn, for example, has by a single method "converted" over two hundred different substances (salts, elements, etc.) into colloids. Of course, different substances are changed into the colloid condition with different degrees of ease, but no decisive effect of the chemical nature of the substance whose dispersion is attempted has as yet been discoverable.

Nor is the chemical nature of a dispersion medium of fundamental significance in determining its ability to maintain a second substance in the colloid condition. Even Graham knew that different dispersion media could mutually displace each other without destroying the colloid state. He was able to replace the water of a silicic acid gel with alcohol, with sulphuric acid, etc. And while the first known metallic colloids were hydrosols, many metallic organosols (metallic colloids in various organic dispersion media) have recently been prepared. Among these are the sols of the alkali metals which cannot even exist in water (The Svedberg).

Neither is the suspensoid or emulsoid character of a colloid

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determined by any perticular chemical properties of the disperse phase. There exist inorganic as well as organic suspensoids. Generally speaking, the emulsoid states are more common than the suspensoid, in the case of the albumins, for example; but suspensoids are also found among these, as shown by their ready precipitability through traces of electrolytes, by their low internal friction, etc. (see pp. 12, 13). As P. P. von. Weimarn has shown in his fundamental researches, the same substance may be obtained either in the suspensoid or emulsoid state (as a jelly) depending upon the conditions of its preparation. One and the same substance may also exhibit either a suspensoid or an emulsoid character depending upon the nature of the dispersion medium as Freundlich and Neumann have found in the case of dyes (see p. 56).

Finally, one and the same substance may appear under different circumstances either as a crystalloid or a colloid. We need but recall the crystallization of albumin or, on the other hand, the production in colloid form of materials usually known only as crystalloids, such as common salt.[1] P. P. von Weimarn (*l.c.*) recently showed that mere change in the concentration of the components of a reaction mixture sufficed to precipitate them either in colloid or crystalloid form. These facts show clearly the fundamental independence of the colloid (and crystalloid) state, of the special chemical properties of the substances involved.

Obviously, the growing acquaintance of investigators with new colloid materials could not but lead them gradually to recognize that colloid properties were not confined to specific chemical substances. The attempts of P. Rohland[2] in 1907 to tabulate colloid materials showed clearly how impossible was such a chemical viewpoint. The result was entirely unsatisfactory, for the table included not only a heterogeneous lot of chemical substances, but was incomplete. Conversely, however, it demonstrated the impossibility of coördinating satisfactorily chemical composition with colloid properties and brought home the fact that all materials may occur in the colloid state. But while this view was already beginning to be recognized in 1905 as a necessary conclusion to be drawn from the rapidly increasing list of colloid materials[1] it should be emphasized that P. P. von Weimarn (1906) was the first to express clearly and emphatically on the basis of these findings that *the colloid, like the crystalloid, is a universally possible state of matter.*

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[1] C. Paal, Ber. d. D. chem. Ges., **39**, 1436, 2859, 2863 (1906).
[2] P. Rohland, Koll.-Zeitschr., **1**, 201, 289 (1907); **2**, 53 (1907).

Although experiment shows the colloid state to be independent of the chemical composition of the phases, this does not of course mean that the properties of the dispersoids may not change with varying chemical composition of the phases. Examples have already been given which show that one and the same chemical substance may assume different types of dispersion with different kinds of dispersion media. The usual view of this behavior which holds the "chemical nature" of the phases responsible for the observed changes, may easily lead to error, for it is not the chemical properties, in other words, the analytical composition and the reactivity which determines whether a substance dissolves as a colloid or molecular dispersoid, but rather the different physical properties such as different "solubility" values, etc., in other words, the free surface energies which bring about the variations in degree of dispersion. Of course, these physical properties, like other properties are in good part dependent upon the chemical composition of the phases, and so change with chemical changes in these. Obviously the stability, reactivity, etc., of a colloid must therefore vary with changes in the chemical composition of the phases concerned. But the chemical relations between disperse phase and dispersion medium characterize the dispersoid just as little as the absorption or liberation of heat which always accompanies chemical processes completely characterize these, even though, as is well known, temperature influences them greatly.

2. Universality of the Colloid State as a Necessary Consequence of Characterizing Colloid Solutions as Disperse Systems.— If it is granted that colloid solutions are merely representatives of disperse systems and that their properties are determined through a degree of dispersion which has both an upper and a lower limiting value, it becomes self-evident that almost any desired material may be prepared in the colloid condition. *For as certainly as all substances have not an unlimited solubility in every solvent, equally certainly can these substances be gotten into a*

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[1] In this connection see Wo. Ostwald, Koll.-Zeitschr., **6**, 184 (1910); R. Zsigmondy, zur Erkenntnis der Kolloide, pp. 170, 171, 175, Jena, 1905.

disperse form provided a proper dispersion medium is chosen. For every substance a second may be found in which the first is "insoluble" or only slightly "soluble." All special problems in "colloid synthesis" consist in finding the experimental means of obtaining the average values in degrees of dispersion that are characteristic of colloids, or of fixing such in passing through a series of progressively changing degrees of dispersion. The question of the "possibility of all substances existing in a colloid state" stands and falls with this recognition of colloid solutions as mere examples of dispersed heterogeneous systems.

It is evident that this classification of colloid and dispersed systems accepts from the start the fundamental independence of the colloid state of the special chemical nature of the phases, for to classify disperse systems according to their degree of dispersion and the state of their phases makes use of no chemical conceptions whatever. On the contrary, it expressly departs from them. In this sense, the assumption of the universality of the colloid state must be termed the first and most essential generalization that may be made regarding this class of dispersed systems. It was therefore included in the conception proposed by Wolfgang Ostwald in 1907 and developed independently of the investigations of P. P. von Weimarn. It should be emphasized, however, that even before the latter's investigations, the accepted *inductive* recognition of the essential independence of the colloid state of chemical composition constituted one of the essential steps which made possible the characterization of colloids as disperse heterogeneous systems.[1]

§18. Isocolloids

The view that the colloid properties of a substance represent only *properties of state* may perhaps be most strikingly demonstrated by considering a class of colloids in which both disperse phase and dispersion medium have the same chemical composition. Among these remarkable colloids are found such as consist of but *one chemical substance*, in other words, their disperse phases and their dispersion medium both consist of the same substance but in different "states." We deal here with systems which are often referred to as "colloid" or "colloidally amorphous," but whose place and relation to the normal or more common colloids has not yet been clearly determined. We shall term these structures in which disperse phase and dispersion medium are chemically isomeric, *isocolloids* (isodispersoids). For those cases in which a single element (in allotropic forms) makes up the colloid system we may reserve the name *allocolloids* (allodispersoids).[1]

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[1] See P. P. von Weimarn and Wo. Ostwald, Koll.-Zeitschr., **6**, 183 (1910); P. P. von Weimarn, *ibid.*, **7**, 155 (1910).

Examples of isodispersoids, more particularly of isocolloids are common in both inorganic and organic chemistry. As mentioned in the practical introduction (p. 1) liquid colloids are especially apt to belong to the group of liquids which behave "abnormally."

In spite of agreement in elementary analysis these structures may, through distillation for example, be divided into several fractions; in other words, they have no "constant" boiling point. Their internal friction often shows a remarkably high temperature coefficient, in other words, varies greatly with changing temperature (mixtures of fluid polymers). Their so-called molar surface energy, that is, the value $V^{2/3}.\gamma$ (V = molar volume = volume of the gram molecular weight; γ = the positive surface tension) is less than that of normal fluids (*associated liquids*).[2] They can at times be separated through centrifuging or even filtration, into a solid or semi-solid phase and a liquid one. They betray their physical heterogeneity optically, for they are turbid, opalescent, give a positive Tyndall effect, and in the coarser dispersoids, a "structure" can be recognized microscopically. Among these systems are found oils, waxes and different varieties of rubber, the higher fatty acids, the fractions of mineral oils which come off at high temperatures,[3] probably molten salts (which according to R. Lorenz[4] are strongly associated), and molten materials of other composition, as phosphoric acid and arsenious acids, which on cooling give rise to glacial forms. The name "glacial" indicates that emulsoid types of isocolloids occur, and our present knowledge would seem to show that the emulsoid type is by far the more common. The so-called "meta forms" of fused materials (which are not to be confused with the meta forms of dissolved materials, like the different stannic acids) are particularly apt to produce jellies and glasses on cooling, as do such typical emulsoids as gelatine and agar. An especially instructive and lucid example is the system styrol-metastyrol, recently investigated by G. Posnjak.[1] Styrol, a hydrocarbon of the composition C_8H_8 polymerizes spontaneously on standing into $(C_8H_8)_n$ which, according to the degree of polymerization, has a jelly-like or glass-like consistency (metastyrol). The polymerization can be followed quantitatively by measuring the internal friction which increases as the polymerization progresses. Interestingly enough this particular example shows what is also true of other substances, that light as well as heat favors polymerization (photopolymerization). When polymerization is complete the product (metastyrol) is hard and glassy, may be pulverized, etc. But the intermediate stages in the polymerization are nothing more than colloid solutions of solid metastyrol in liquid styrol. "If one adds to pulverized metastyrol an equal weight of styrol, the former gradually absorbs the latter. In the process the originally opaque powder becomes translucent and gradually changes into a homogeneous, gelatinous or jelly-like, viscid, transparent mass. If less styrol is added to the metastyrol, say only about a fourth as much of the former as of the latter, a transparent mass results which is not viscid, but glassy" (G. Posnjak, *l.c.*, 14). These changes are entirely analogous to those observed in the swelling of emulsoids. That, on the other hand, fluid colloid solutions may be obtained by employing an excess of the liquid styrol, follows from the unlimited solubility of metastyrol in styrol[2] as observed by G. Lemoine.[3]

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[1] Of the available prefixes, eu, hylo, allo, auto, iso, etc., that of iso is perhaps the best.

[2] For details see the textbooks on Physical Chemistry, for example Wilh. Ostwald, Grundr. d. allgem. Chemie, 4 Aufl., Leipzig, 1909.

[3] For a discussion of their colloid properties see D. Holde, Koll.-Zeitschr., **3**, 270 (1908); Z. f. angewandt. Chem., 2138 (1908); J. Schneider and J. Just, Z. f. Wissench. Mikrosk., **22**, 501 (1905).

[4] R. Lorenz, Z. f. physik. Chem., **70**, 236 (1910).

Sulphur[4] is a typical allocolloid, as are phosphorus and selenium. As is well known, the soft plastic, translucent to transparent[1] form of sulphur obtained by cooling it rapidly has long been called colloid or "colloidally amorphous" sulphur. As the result of many investigations, we have been forced to assume the existence of several more so-called *allotropic* modifications more especially of two *liquid* forms of sulphur, designated as S_λ and S_μ. When pure sulphur is heated one obtains the modification S_λ which is a bright yellow, labile liquid, from the temperature at which the sulphur first melts up to 160°C. If the temperature is further raised the system again becomes viscid and its surface tension again increases. If this melted sulphur is cooled to 100° then as Malus, F. Hoffmann and R. Rothe, A. Smiths, etc.,[2] have shown a second liquid sulphur phase, S_μ makes its appearance which gives rise to the so-called "insoluble" sulphur when the sulphur solidifies. Between 160° and about 270° in the range of the physical irregularities mentioned above, the system is therefore allodispersed and it seems logical to assume that at certain temperatures, a colloid condition is traversed. The physical characteristics observed in the behavior of sulphur remind us in many respects of the behavior of emulsoid colloids.[3]

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[1] G. Posnjak, Das Metastyrol und die beiden Distyrole, Diss., Leipzig, 1910.

[2] The different polymerization or dispersion states of styrol are preserved even when dissolved in a chemically heterogeneous solvent such as carbon tetrachloride. This is proved not only by the fact that, like a typical colloid, metastyrol when in solution, causes no rise in the boiling point, but also by the different reactivity observed in the different stages of polymerization. When a drop of permanganate solution, made alkaline with sodium hydroxide, is added to solutions of liquid styrol, gelatinous styrol and solid metastyrol, having the same percentage concentrations, it is decolorized respectively in 10 seconds, in 40 seconds and 650 seconds (G. Posnjak, *l.c.*, 16).

[3] G. Lemoine, Compt. rend., **125**, 530 (1897); **129**, 719 (1899).

[4] I have previously pointed out the great interest attached to a consideration of the allotropic forms of sulphur from a colloid-chemical standpoint, Koll.-Zeitschr., **7**, 172 (1910).

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[1] Concerning perfectly "transparent" sulphur see P. P. von Weimarn, Koll.-Zeitschr., **6,** 250 (1909).

[2] An extended discussion of the work done on sulphur up to 1902 may be found in Wilh. Ostwald, Lehrb. d. allg. Chem., 2, Aufl, II, **2,** 449. See also the recent extensive papers of A. Smiths and his coworkers, Zeitschr. f. physik. Chem., **42,** 469 (1903); **52,** 602 (1905); **54,** 276 (1906); **57,** 685, 692 (1907); **61,** 200 (1907); F. Hoffmann and R. Rothe, *ibid.*, **55,** 113 (1906); **59,** 448 (1907); H. R. Kruyt, *ibid.*, **64,** 513 (1908) where extensive references to the literature may be found; **65,** 486 (1909), etc.

[3] I purpose publishing details regarding these analogies elsewhere. Here I would only point out that sulphur melts bring to mind the *critical fluid mixtures* such as those of butyric acid and water, a fact which seems not previously to have been noted. Thus the viscosity curves in the temperature ranges where an anomalous behavior is noted [see L. Rotinjanz, Z. f. physik. Chem., **62,** 609 (1908)] are identical in form with the corresponding friction curves of aqueous critical fluid mixtures [J. Friedländer, *ibid.*, **38,** 430 (1901)]. Attention should also be called to the nonconclusiveness of the view that both fluid phases "cannot" exist in equilibrium above and below the "transition" point (about 160°) because this would contradict the phase rule [see especially H. R. Kruyt, *l.c.*]. As a matter of fact the apparently *unlimited stability* of critical fluid mixtures as proved by Friedländer's careful studies seems to indicate that "real" equilibria and not simply "dynamic" retardations exist in the case of sulphur also. Those investigators, who assert that the existence of true equilibria would contradict the phase rule, forget that this rule holds only *if the nature of the phases is the same throughout their entire mass*, or, to quote Gibbs himself, only "if the changes of the shares of energy and entropy which arise from the surfaces between the heterogeneous masses, are so small in comparison with those which arise from these masses themselves that they are negligible. In other words, we will exclude any consideration of the effects of capillarity." [Thermodynamische Studien, 75, Leipzig, 1892. See especially pp. 89 and 90 where the reasons for the limitation mentioned above are given in greater detail.] But this assumption of Gibbs as used in his general considerations of the phase rule is, of

As shown by the photographic investigations of O. Bütschli[1] and A. Wigand,[2] highly dispersed *solid* systems of sulphur may also be produced. It would be of interest to extend these investigations into the ultramicroscopic realm of the colloids. This has been done by H. Siedentopf[3] for phosphorus which shows analogous separation phenomena under the influence of intense light.[4] White phosphorus, as is well known, is coverted into red, by light. The intense light of a so-called "cardioid" ultramicroscope accomplishes this in a few seconds. Ultra-microscopically, a solidified drop of white phosphorus at first appears "empty," but almost instantly, upon illumination, white submicrons appear. These grow and combine through tendril-like extensions into a kind of network, and finally become red. According to these investigations white phosphorus, with a trace of red phosphorus undoubtedly represents a solid, at first perhaps, semi-solid allocolloid.

§19. Multiplicity of the Colloid State of One and the Same Substance. Example: Colloid Ice

As a further evidence of the fundamental independence of the colloid state of the chemical character of the substance, and as an

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course, not true as I have repeatedly emphasized, and as Gibbs himself has said, when we deal with disperse and more especially, colloid systems. Gibbs started with the assumption that we could neglect that part of the energy, etc., which originates in the *surfaces* between the heterogeneous masses. Such an assumption is fully justified in many cases and for many purposes, or whenever the masses are large; but when the masses are formed in or between materials of different nature or state, or are at the instant of formation infinitely small, such an assumption becomes unreliable, for now the surfaces become infinitely large as compared with the masses. In answer to the question as to whether the phase rule holds for colloids, we may say, that a phase rule which recognizes only concentration, pressure and temperature as variables, is not going to be valid, but an elaborated one in which the degree of dispersion of the system is added will be. The same is true in dealing with electrically charged disperse phases, in which account must be taken of the influence of electrical energy upon the equilibrium of the system; for as is well known, the latter is not, or at least not always, a function of the mass of the charged phase. Regarding the validity of the phase rule in colloid systems see J. M. van Bemmelen, Die Absorption, Ges. Abhandlgn., 347, Dresden, 1910; A. Mittasch, Zeitschr. f. physik. Chem., **34,** 495 (1900); G. Galeotti, *ibid.*, **54,** 727 (1905); P. Pawlow, *ibid.*, **75,** 48 (1910). In the last-named paper which appeared while these paragraphs were in press, the phase rule is broadened as suggested above.

[1] O. Bütschli, Untersuchungen über Strukturen, Leipzig, 1898; Die Mikrostrukturen des estarrten Schwefels, Leipzig, 1900.

[2] A. Wigand, Zeitschr. f. physik. Chem., **72,** 752 (1910).

[3] H. Siedentopf, Ber. d. dtsch. chem. Ges., **43,** 692 (1910).

[4] As in well known, sulphur also suffers an allotropic change under the influence of light (Daguin, Lallemand, Berthelot, Rankin, etc., see H. R. Kruyt, *l.c.*, 543 (1908).

example of the multiplicity of colloid phenomena that may be exhibited by one and the same substance, we shall consider the possible colloid forms of water, and those which have actually been prepared. As follows from the chapters on the influence of the degree of dispersion and of the type of the dispersed material upon the colloid state, the same chemical compound may give rise not only to one, but to a large number of colloid systems. If our view is correct, that only a certain intermediate degree of dispersion gives the property of a colloid, then it should be a matter of indifference, in the case of water, with which form we begin. From it we should be able to prepare all its various colloid states. That such is possible seems proved by recent investigations (G. Quincke,[1] P. P. von Weimarn and Wo. Ostwald,[2] H. Schade[3]).

1. Isocolloids of H_2O.—Let us commence with the isocolloid state. The following possibilities exist:

(*a*) Solid ice (dispersion medium) + water-vapor bubbles of colloid dimensions (disperse phase). Coarsely dispersed systems of this character, as the turbid or milky-white ice (milk ice) produced by refrigerating machines, are well known. It is probable that a more exact study of the relation between degree of turbidity or diameter of the bubbles and the conditions prevailing during preparation of the ice will acquaint us with systems showing a colloid degree of dispersion.

(*b*) Solid ice (dispersion medium) + liquid droplets of colloid diameter (disperse phase). Considerations analogous to those discussed in the preceding paragraph hold for this case. G. Quincke (*l.c.*) regards it as the most general structure of solid, "amorphous" ice.

(*c*) Solid ice (dispersion medium) + solid ice of a colloid degree of dispersion (disperse phase). That such systems exist is proved by the investigations of G. Tammann,[4] who, as a matter of fact, recognizes three or four different modifications of solid ice. According to G. Quincke (*l.c.*) the forms of ice described in the previous paragraphs, may, by lowering the temperature, by freezing at different rates, etc., be converted into the system discussed here.

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[1] G. Quincke, Drude's Ann. d. Physik., **18,** 11 (1905).

[2] P. P. von Weimarn and Wo. Ostwald, Koll.-Zeitschr., **6,** 181 (1910).

[3] H. Schade, Koll-Zeitschr., **7,** 26 (1910). See also the extended discussion of this theme in Trans. Faraday Soc., **6,** 71–129 (1910).

[4] G. Tammann, Zeitschr. f. physik. Chem., **69,** 569 (1910); **72,** 609 (1910); Zeitschr. f. anorgan. Chem., **63,** 283 (1909) where may be found further references to the literature on the different modifications of ice.

(*d*) Fluid water (dispersion medium) + water-vapor bubbles of colloid dimensions (disperse phase). Highly dispersed systems of this type are represented by the chemically homogeneous fluids near their critical vaporization temperatures. Their fine turbidity or strong opalescence, their varying density, etc., etc., betray their colloid character.[1]

(*e*) Fluid water (dispersion medium) + fluid water droplets of colloid dimensions (disperse phase). As is well known, water belongs to the strongly associated liquids, so that the formation of complexes and of polymeric molecules (polyhydrols) more especially at lower temperatures has often been called upon to explain its anomalies in behavior.[2] Since modern theorists hold that this polymerization may be so great that they speak of the formation of "droplets" of the polymer in the non-associated liquid, it is easy for us to assume that colloid degrees of dispersion may be reached. H. Schade (*l.c.*) has, as a matter of fact, developed such a colloid-chemical theory of the constitution of water, according to which its behavior in many directions is shown to be analogous to that of well-recognized colloids. The observation of P. P. von Weimarn (*l.c.*) that water suddenly cooled (by mixing with liquid air) is at first soft and viscid, brings to mind the behavior of melted sulphur, when this is cooled to 100°C.

(*f*) Fluid water (dispersion medium) + colloidally dispersed solid ice (disperse phase). It cannot be definitely decided whether highly dispersed examples of this type really exist. Snow in water would represent a coarsely dispersed system of this type.

(*g*) Water vapor (dispersion medium) + water droplets of colloid dimensions (disperse phase). Examples of this are found among the critical phenomena as in the liquefaction of water vapor. Such structures, usually called mists or fogs, play a great part in cosmic physics, where they are known as clouds, or when in a coagulated state, as *rain* (P. Pawlow).[3]

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[1] See, for example: J. P. Kuenen, Die Zustandsgleichung, 34, Braunschweig, 1907.

[2] See H. Schade for references to the literature on this subject.

[3] P. Pawlow, Koll.-Zeitschr., **8** (1911). I also pointed out that these cosmic structures are examples of dispersed or colloid systems [Koll.-Zeitschr., **1**, 291, 331 (1907), and in the first German edition of this book, 96 (1909)].

(*h*) Water vapor (dispersion medium) + colloidally dispersed ice (disperse phase). Such systems are obtained as fine *snows* when fogs are rapidly cooled below their freezing point. Their optical properties, which remind us of the Tyndall effect of colloid systems, are observable on winter nights, when the moon has a halo. The fact that in winter we deal with fine particles of *solid* ice explains why the halo is then more marked than in summer when the mists are liquid in character.

2. Chemically Heterogeneous H_2O Colloids.—When only the *disperse* phase consists of water, while the dispersion medium is another substance, then as in the case of the water-isocolloids eight colloid systems are possible. The water must of course be insoluble in such systems, or at least but slightly soluble, otherwise molecular dispersoids result. It is an easy matter to take up these eight possibilities, to coördinate them with what was said before, and to find examples for the different types. Of especial interest are the ice colloids of the composition liquid + gas, liquid + liquid and liquid + solid, in other words, the aqueous colloid "foams," the aqueous emulsoids and the ice suspensoids. In the known examples of the first two of these classes, we seem again to be dealing as a rule, with *complex* dispersoids, in that the gas bubbles obtained, say, by sudden diminution of pressure in an alcohol-water mixture (champagne or charged water constitute crude examples), usually consist of a mixture of several gases (water vapor, alcohol vapor, air, carbon dioxide, etc.). More decisive experiments could, of course, be arranged.[1] The commonest illustrations of highly dispersed water are also found in complex systems, as in phenol-water, mineral oil-water, etc. Such systems, as a rule, are rather unstable, their instability increasing with the *purity* of the liquids employed. The stability may be greatly increased by adding substances like saponin, soap, gelatine, etc.

Finally, highly dispersed colloid systems of the composition liquid + solid, in other words, ice suspensions and ice suspensoids, have recently been prepared. Such systems are obtained when organic liquids in which water is only slightly soluble in molecular form are rapidly cooled while thus saturated with water. Ether, xylol and especially chloroform have been found suitable for this purpose. Depending upon the amounts of water dissolved, the rate of cooling, etc., systems of varying degrees of dispersion are produced, the turbidity of which is the less, or the opalescence (yellowish-blue) of which is the greater, the more highly dispersed the ice phase which separates out. Under favorable conditions, these mixtures coagulate spontaneously after standing some 40 minutes,[1] in the form of snow-white flakes or "cream," which rise to the surface of the liquid. The addition of certain substances like resins, the salts of fatty acids, etc., greatly increases both stability and degree of dispersion. By rapidly chilling chloroform saturated with water to -30°, ice dispersoids may be obtained which pass through filter paper (Schleicher and Schüll, 602, extra hard). This indicates that the ice particles are less than 1μ in diameter, in other words, that they are already within the colloid range of dispersion.

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[1] For some observations on highly dispersed aqueous foams see Wo. Ostwald, Koll-Zeitschr., 1, 333 (1907).

The possible colloid forms of water are not exhausted by these sixteen types. It was pointed out on pp. 35, 44, etc., that colloid systems assume different properties with differences in the relative proportions of disperse phase and dispersion medium. This is especially true when very dilute colloids are compared with concentrated ones. Thus while many colloids with a small content of disperse phase show suspensoid properties, the more concentrated systems often have emulsoid properties, they are, in other words, jelly or glass-like. One suspects that he is here dealing with a general law and so looks for such in the extreme concentrations of ice colloids. Thus J. Alexander[2] has shown that "ice creams" consist of numerous highly dispersed ice crystals in the dispersion medium, cream, to which a trace of gelatine is often added. The bulk of the ice crystals is so great as compared with that of the dispersion medium, that as in the case of fine, moist sand, the dispersion medium covers the solid dispersed particles with a thin but coherent envelope.

So far as structures of the composition liquid + liquid are concerned, we may direct attention to the experiments of Wa. Ostwald[3] which indicate the possible existence of emulsions in which the *disperse (aqueous) phase is present in excess.* Foams may also occur in these two modifications. We may have fluid structures made turbid by minute bubbles (see above) or "stiff foams" consisting chiefly of vapor, held together by a small amount of fluid dispersion medium, as in well-whipped saponin, albumin, beer, etc. It is characteristic of most of these systems that they are fairly stable only when certain third substances are present.[1]

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[1] See P. P. von Weimarn and Wo. Ostwald, *l.c.*

[2] J. Alexander, Koll.-Zeitschr., **4**, 168 (1909); **5**, 101 (1909).

[3] Wa. Ostwald, Koll.-Zeitschr., **6**, 103 (1910).

In concluding these paragraphs it should be noted that even with this long list all the theoretical possibilities are not yet exhausted. For example, there are *several* solid modifications of ice known, any of which may appear, theoretically at least, as disperse phase or dispersion medium; and when we consider compounds or elements whose polymorphism is still greater, as in the numerous solid, liquid and gaseous modifications of sulphur, the number of disperse and colloid states of one and the same substance, which are theoretically possible, becomes almost limitless.

§20. The Concept of Colloid-chemistry

The most important deduction from the previous paragraphs is that it is no longer appropriate to contrast colloid *substances* with crystalloid *substances* as though the condition were dependent upon the specific chemical properties of the material. *Colloid-chemistry is not the study of colloid materials but that of the colloid state of materials* (Wo. Ostwald, 1908). "Colloid" is not a chemical entity like salt, acid, base, oxidizing or reducing agent, but is expressive of certain *physical* elements like mechanical heterogeneity. The concept "colloid" does not even correspond to that of "precipitate" since only special *forms* of precipitates may be termed "colloid." Nor may "colloid" substances be discussed as we discuss "radio-active" substances, for radio-active properties are more closely associated with certain chemical compounds showing definite properties (high atomic weight, etc.), than are the colloid. Like considerations hold when we try to parallel the colloid condition with the "liquid crystalline," though as our knowledge has increased we have found the latter state less and less directly connected with definite chemical compounds.[1] In the same sense "colloid phenomena" are not to be regarded as due to the properties of any special class of materials but rather as characteristic of *any* material observed in the colloid state. The difference between these two definitions will perhaps be clearer if we compare colloid-chemistry with thermo-chemistry. Just as the latter is not a study of "warm" and "cold" materials, but a study of the *thermal condition* of the material and its changes, so colloid-chemistry is not a description of individual colloid materials but treats of the properties of which colloid systems are but examples. Colloid-chemistry deals with *the relations of the surface energies to other kinds of energy as shown in an especially characteristic way in dispersed heterogeneous systems.* Thus viewed, colloid-chemistry appears as a branch of physical chemistry coördinated with electro-, thermo-, photo-, radio-chemistry, etc., in other words, with sciences which also treat of the relations of one kind of energy to others. Attempts have been made to express this by calling it *capillary chemistry* (Freundlich), *strato-chemistry* (Drucker), *micro-chemistry* (Wilh. Ostwald), etc. Since philological and practical objections may be raised against most of these terms the historically justified and useful one of "colloid-chemistry" will be retained in these pages.

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[1] Regarding this point and the making and breaking of emulsions in general, together with a discussion of its technological and scientific applications, see Martin H. Fischer and Marian O. Hooker, Fats and Fatty Degeneration, New York, 1917.

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[1] We need but recall the "inorganic" liquid crystals recently discovered. See H. Stoltzenberg and M. E. Huth, Z. f. physik. Chem., **71**, 641 (1910), etc.

PART II

SPECIAL COLLOID-CHEMISTRY

A. THE GENERAL PHYSICO-CHEMICAL PROPERTIES OF COLLOIDS

CHAPTER V

MECHANICAL PROPERTIES OF COLLOID SYSTEMS

I. RELATIONS OF VOLUME AND MASS IN COLLOIDS

§21. Volume and Density Relations in Colloids

1. Volume Relations of Colloid Systems.—*Compressibility.*—In one of the previous sections (§14) reference has been made to the fact that the surface between two phases (for example the surface between a liquid and a gaseous phase) has properties distinctively its own. These peculiar surface properties do not extend much below the surface, not deeper than the "sphere of molecular attraction." But in spite of the thinness of this layer it does not resemble a mere shell, in other words, it is not separated from the rest of the phase by a sharp line. Mathematical considerations[1] would seem to indicate that there is a continuous change of properties within this layer, extending asymptotically into the depth of the phase. In addition to the fact that the surface of contact is the seat of surface energy we must also assume that its hydrostatic pressure and the related properties of volume and density differ from these same properties as exhibited by the interior of the phase. We have also pointed out how in coarsely disperse systems these differences can be demonstrated only with great difficulty. But the slight differences observed in coarsely disperse systems add up to considerable values in systems which have great areas of "surface contact." Especially is this true in the disperse heterogeneous systems where a great specific surface is found with great absolute surface. The relation between specific surface and volume is established by the *capillary or curvature pressure* (Krümmungsdruck).

Consideration of the progressive change in the properties of the surface and the effects of capillary pressure lead to the conclusion that the volume of the dispersoid need not be equal to the sum of the volumes of dispersion medium and of disperse phase.

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[1] See for example van der Waals and Kohnstamm, Lehrb. der Thermo-dynamik, 1, 64, as well as Hulshof from whose works we have quoted.

The observed values are usually less than the arithmetic mean. This is in harmony with the assumption that the effect of positive capillary pressure generally outweighs that of the negative.[1] The amount of this contraction besides being a function of the positive capillary pressure is evidently a function of the compressibility or expansibility of the two phases in the sense that a great coefficient of compression or expansion will favor change in volume.

It seems important, therefore, to consider the compression coefficients of colloid solutions. Theoretically, three compressibilities must be considered in a colloid (or in any dispersoid): the compressibility of the dispersion medium, the compressibility of the disperse phase, the compressibility of the system as a whole. The first and third of these can be measured by physical methods, the value of the second may be calculated from the other two. Of greatest immediate interest is a comparison of the compressibility of a colloid solution with that of the pure dispersion medium. One anticipates that the compressibility of the colloid solution will be *smaller* than that of the pure dispersion medium, and that it will decrease as the concentration of the colloid increases. That these relations will be more complicated in emulsoids than in suspensoids is also to be expected. The curve expressing the relation between concentration and compression of emulsoids will probably not be a straight line as in suspensoids. The fact that it is not a straight line in molecular- and ionic-disperse systems already indicates this; for as the investigations of Röntgen and Schneider,[2] H. Gilbaut[3] and others have shown, this function approximates a hyperbolic curve diverging more and more from a straight line with increasing concentration (see Fig. 20). Fig. 17 shows the relation between compressibility and concentration of NaCl according to the experiments of H. Gilbaut. A similar behavior is to be expected for the emulsoids because of their close relation to the molecular dispersoids.

One would also expect that electrically charged or ionized colloids would reduce the compressibility of the pure *dispersion* medium more than such not so charged, for according to Guinchant[4] the compressibility of water is less reduced through addition of a non-electrolyte than of an electrolyte.

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[1] See p. 91.

[2] W. Röntgen and Schneider, Wiedemann's Ann. d. Physik., **29**, 165 (1886).

[3] H. Gilbaut, Z. f. physik. Chem., **24**, 385 (1897).

[4] Guinchant: Compt. rend., **132**, 469 (1901).

Of the available determinations on colloids those of G. de Metz[1] merit special attention. Table 3 gives a selection from his careful measurements. For comparison the values of water and some other non-colloid solutions are appended. The table shows that at least as far as the emulsoids which have thus far been studied are concerned the compressibility of colloids is not *essentially* different from that of other non-colloid liquids. The compressibility of collodion is twice that of water, but crystallized benzene has also an abnormally high coefficient. In the case of hydrosols we find, with the exception of setting gelatine, that the coefficient of compressibility is *lower* than that of the pure dispersion medium which again is analogous to the behavior of molecular dispersoids. This also seems to apply to benzene-sols, as comparison of the values for pure benzene and for a solution of Canada balsam in benzene indicates.

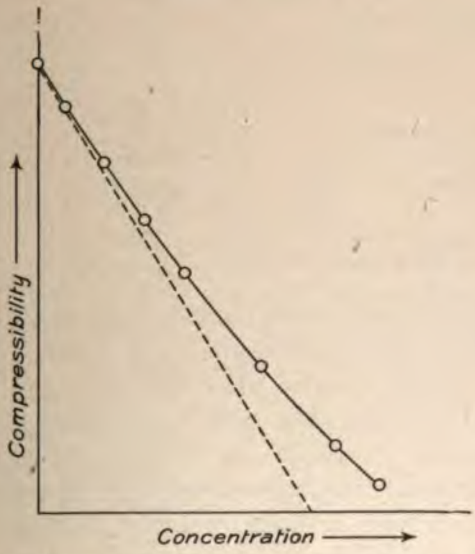

FIG. 17.—Compressibility of NaCl solutions in concentrations varying between 0 and 26.22 percent. (According to *H. Gilbaut.*)

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[1] G. de Metz, Wiedemann's Ann. d. Physik., **35,** 497 (1888); see also G. Quincke, *Ibid.*, **19,** 401 (1883); E. H. Amagat, Ann. chim. et phys. (5), **11,** 535 (1877).

TABLE 3.—COMPRESSION COEFFICIENTS OF COLLOID SOLUTIONS
(From G. de Metz)

Substance	Specific gravity	Compression coefficient (absolute) k.10^{-6}
Non-gelatinous glue	1.053 (14.8°)	44.337 (12.18°)
Gum arabic in water	1.041 (14.0°)	44.593 (14.84°)
Gelatinizing glue*	1.005 (18.2°)	48.388 (11.67°)
Canada balsam in benzene	0.950 (15.0°)	57.205 (14.90°)
Duplex collodion	0.807 (15.0°)	97.433 (14.85°)
	1.345 (14.5°)	25.509 (14.64°)
Water	1 (15.0°)	47.430 (12.58°)
Sugar in water	1.350 (13.5°)	20.827 (14.80°)
Metaphosphoric acid in water	1.545 (13.5°)	19.663 (14.68°)
Glycerine	1.245 (16.5°)	22.128 (14.92°)
Benzene (crystallized)	0.882 (18.2°)	74.609 (14.77°)
Liquid paraffine	0.860 (17.0°)	62.865 (14.84°)

*The compressibility changes with time.

The behavior of gelatinizing glue is particularly interesting, for its compressibility *decreases* with time. According to G. de Metz, a 2 percent solution showed when first measured a compressibility of 51.42 ($\times 10^{-6}$); three hours later this decreased to 49.73, and ten days later to 48.44. In other words, as gelation proceeded the compressibility approached more and more the value of the pure dispersion medium (water). This observation is of interest in its application to the theory of gelation in emulsoids.

Other compressibility determinations have been made by C. Barus.[1] Barus measured the height of liquids in capillary glass tubes at various pressures. The compressibility is equal to the decrease in height divided by the total height of the liquid in the capillary tubes $\left(=\frac{1}{L}\right)$. Table 4 gives some of his results.

These figures[2] show that compressibility differences between colloids and their pure dispersion medium are *slight*, especially when compared with the corresponding variations observed in

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[1] C. Barus, Silliman's Amer. Journ. Science (4), **6**, 285, (1898); (3), *Ibid.*, **41**, 110 (1891), Compressibility of Glass.

[2] For further tables, for example, on the compressibility of coagulated albumin, etc., see the original work of C. Barus.

TABLE 4.—COMPRESSIBILITY OF COLLOID SOLUTIONS
(After C. Barus)

Water $T = 23^\circ$; $L = 17.4$ cc.; $p =$ Atm.		**Natural egg-albumin** $T = 22^\circ$; $L = 12.3$ cc.; $p =$ Atm.	
p	$\frac{1}{L}$	y	$\frac{1}{L}$
0	0.0000	0	0.0000
83	0.0037	81	0.0039
160	0.0075	128	0.0061
226	0.0108	191	0.0093
Water $T = 100^\circ$; $L = 18.1$ cc.; $p =$ Atm.		**Gelatine 10 percent** $T = 100^\circ$; $L = 21.1$ cc.; $p =$ Atm.	
p	$\frac{1}{L}$	p	$\frac{1}{L}$
0	0.0000	0	0.0000
83	0.0046	116	0.0058
180	0.0098	211	0.0100
244	0.0133	282	0.0133
Ether $T = 29^\circ$; $L = 14.37$ cc.; $p =$ Atm. $(p = 20)$		**5 Percent rubber in ether** $T = 23.9^\circ$; $L = 7.72$ cc.; $p =$ Atm. $(p = 20)$	
p	$\frac{1}{L}$	p	$\frac{1}{L}$
20	0.0000	45	0.005
100	0.0137	123	0.017
200	0.0291	195	0.027
300	0.0423	286	0.038
400	0.0540		
$T = 100^\circ$; $L = 16.85$ cc.; $p =$ Atm. $(p = 10)$		$T = 100^\circ$; $L = 8.93$ cc.; $p =$ Atm. $(p = 10)$	
p	$\frac{1}{L}$	p	$\frac{1}{L}$
10	0.0000	57	0.021
100	0.0357	148	0.051
200	0.0653	221	0.071
300	0.0876	228	0.088
400	0.1060		

molecular dispersoids. They show clearly, however, that gelatine sol, for example, at 100° is about 10 percent less compressible than pure water (see Fig. 18). This difference lies well beyond any possible experimental error. A series of measurements by H.

Gilbaut[1] on the compressibility of a 30 percent potassium iodide solution at 20° is introduced for comparison.

A more thorough investigation of the compressibility of suspensoids and emulsoids would be interesting, especially as dependent upon concentration and temperature[2] but more exact methods than those employed by C. Barus would have to be used, like those of Amagat and Gilbaut.

The compressibility of gels cannot be discussed until their general properties have been taken up.

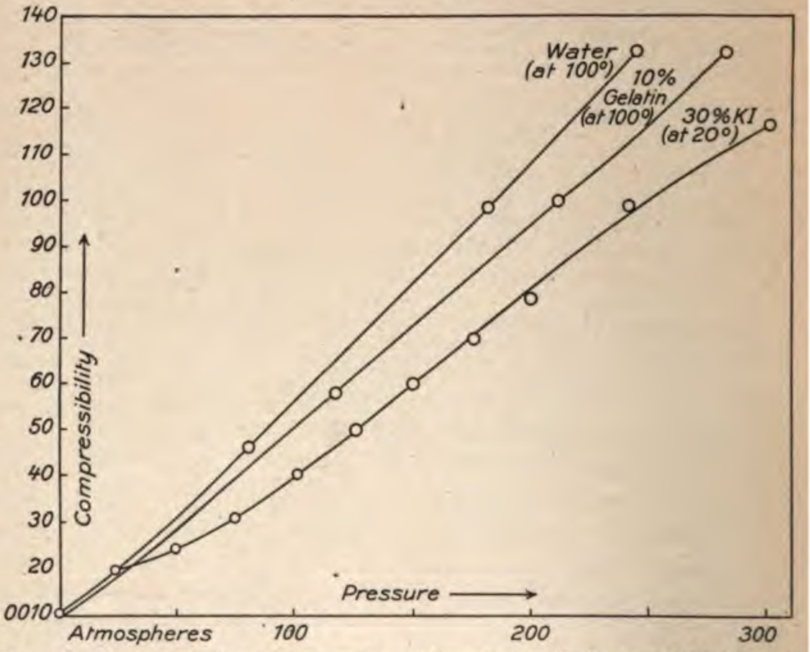

FIG. 18.—Compressibility of dispersoids. (According to *C. Barus* and *H. Gilbaut*).

2. Density and Space Relations in Colloid Systems.—That the density (weight/volume) or specific volume (volume/weight) of colloid systems must have values other than the arithmetic mean of the values of dispersion medium and dispersed phase follows from the existence of capillary pressure and from the compressibility relations. The change in density may be calculated in advance by the method of Wilhelm Ostwald[1] if a positive capillary pressure (the result of positive or contractile surface tension) is present and size of the particles, surface tension and compressibility are known. Such calculations show that drops of water 3μ in diameter are 0.00005 times denser than water in bulk. As previously pointed out (p. 73) this apparently insignificant value increases rapidly with further subdivision so that drops of water 0.03μ in diameter, possessing, in other words, a colloid degree of dispersion have a density 0.5 percent greater than water in bulk. From this it follows that similar changes of density must be observable whenever coarsely dispersed or nondispersed systems pass into colloid ones, as in the "solution" of colloids or the closely related phenomena of swelling in emulsoids.

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[1] H. Gilbaut, *l.c.*, 422.

[2] The relation between compressibility and temperature in gelatine solutions has also been studied by Barus, but no values were obtained which in his judgment permitted of positive deductions regarding any special behavior of colloid solutions.

As a matter of fact such changes have been frequently found. The experiments of G. Rose[2] may be cited for changes of density in *suspensoid* systems. This investigator found the following values for gold of different degrees of dispersion:

Molten and compressed	19.33
Precipitated with oxalic acid	19.49
Precipitated with ferrous sulphate	19.55 to 20.71

Ferrous sulphate precipitates gold as a very fine powder, oxalic acid in the form of tiny platelets. Similarly, barium sulphate in lumps showed a density of 4.48; in precipitated form one of 4.521 and 4.535. The measurements carried out by J. P. Cholodny[3] on colloid selenium and silver showed similar though smaller differences. As has already been mentioned, the compressibility of the substances themselves is an essential factor in these investigations of the influence of dispersion on density, and since this compressibility is itself but small any variations observed in it can also only be slight.

In studying the influence of solid suspended particles upon the density of a liquid, one encounters complicated relations.[4] We can only say that the calculated density taken as the arithmetic mean approaches the observed value more and more with increasing degree of dispersion of the solid. This rule, however, applies only to average degrees of dispersion, for decided deviations are found when dealing with substances in a state of colloid subdivision. It would be of interest to have available a series of measurements showing the dependence of the density of a dispersoid upon the degree of dispersion.

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[1] Wilhelm Ostwald, Grundriss d. allg. Chem., **4**, 533 (1910 Edition).

[2] G. Rose, Poggendorf's Ann., **73**, 1 (1848).

[3] J. P. Cholodny, Kolloid-Zeischrift, **2**, 19, 340 (1907).

[4] See, for example, the recent work of B. Löffler, Drude's Ann. d. Phys., **23**, 3 (1907).

Measurements of density changes in *emulsoid* systems are more numerous. By direct observation in a dilatometer, H. Quincke[1] found that the system, dried egg albumin-water (100 grams albumin + 163.9 cc. water) showed a decrease in volume amounting to 4.175 cc. after thirty-six hours. In another instance (100 grams albumin + 144.77 cc. water) a contraction of 5.168 cc. took place. In the latter instance the contraction in volume amounts to more than 3.5 percent. The densities of dried and hydrated cartilage were observed to be as follows: the calculated values in the table are the arithmetic means.

Dried	Hydrated (observed density)	Hydrated (calculated density)
1.407	1.0892	1.0826
1.368	1.1124	1.1090

Chr. Lüdeking[2] among others has made similar investigations on gelatine gels, and H. Rodewald[3] on starch. The following table gives some of their findings.

TABLE 5

	Observed density	Calculated density	Difference
10 percent gelatine	1.069	1.0412	0.028
20 percent gelatine	1.135	1.203	0.032
50 percent gelatine	1.242	1.206	0.036

If the volume of 1 cc. of water after contraction is calculated from these figures the following values are obtained:

For 10 percent gelatine	0.96069 cc.
For 25 percent gelatine	0.93748 cc.
For 50 percent gelatine	0.90201 cc.

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[1] H. Quincke, Pflüger's Arch., **3**, 332 (1870); still earlier observations are recorded by W. Schmidt, Poggendorf's Ann., **114**, 337 (1861).

[2] Chr. Lüdeking, Wiedemann's Ann. d. Physik., **35**, 552 (1888).

[3] H. Rodewald, Zeitschr. f. physik. Chem., **24**, 193 (1897).

The assumption has here been made that only the water and not the gelatine has been compressed, which is probably not strictly true.

These experiments show that the *contraction increases with the concentration of the system.* This is even more evident from the experiments of H. Rodewald on the decrease in volume when starch absorbs water (see Table 6 and Fig. 19).[1] Here also the contraction of volume increases *absolutely* with the concentration, only the concentration has in this case not been referred to the disperse phase (starch) but to the dispersion medium (water).

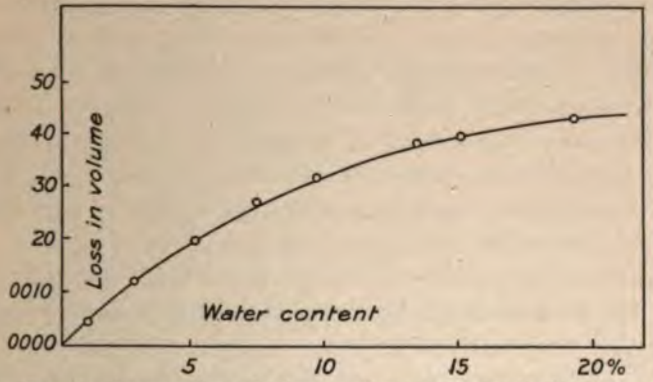

FIG. 19.—Relation between loss of volume and water content in absorption of water by starch. (Calculated from measurements by *H. Rodewald.*)

TABLE 6.—CONTRACTION IN VOLUME OF THE SYSTEM STARCH-WATER
(Referred to the Volume Contraction of Starch, after H. Rodewald)

H_2O content of starch in percent	Volume relation of starch (volume/weight)	Volume contraction of starch. Difference between volume relations of dried and of moist starch
0.0	0.72585	
1.17	0.72124	0.00461
2.69	0.71319	0.01266
5.02	0.70486	0.02099
7.40	0.69881	0.02704
9.70	0.69344	0.03241
13.41	0.68727	0.03858
14.95	0.68555	0.04030
19.24	0.68151	0.04434
Maximum	0.67273	0.05312

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[1] The values in the table and the figure have been partly recalculated from Rodewald's measurements.

But Fig. 19 also shows that the greatest *relative* contraction occurs when the water content is at a minimum, in other words, the first traces of moisture suffer a relatively greater contraction than the subsequent ones. This is indicated by the curve which is concave toward the abscissa. It should be emphasized that J. M. van Bemmelen pointed out all these facts years ago in discussing water absorption by inorganic gels.[1]

In considering molecular and supermolecular dispersoids attention might be called to the contractions in volume occurring in the ordinary process of solution. The striking "electrostrictures" which take place when electrolytes go into solution should be especially mentioned.[2] Whether *increases in volume* dependent purely upon mechanical effects are of general occurrence in dispersed systems cannot be definitely stated at the present time, for in dispersive processes which are associated with increase of volume, as in the solution of ammonium salts in water, both chemical and electrochemical changes occur in the dispersed phase.

3. The Concentration Function of Density in Colloid Systems.—The few observations thus far available on the relation of density to concentration in colloids show an interesting *difference between suspensoids and emulsoids*. The figures of S. E. Linder, H. Picton[3] and G. Quincke[4] which are given in Table 7 and Fig. 20 show that in suspensoid systems the change in density is strictly proportional to the concentration; in other words, the function, density-concentration, is linear and the corresponding curve a straight line. Fig. 20 shows how accurately this applies to the sol of arsenious trisulphide. In contrast herewith, the density-concentration curve of gelatine shows a decided curvature, concave toward the ordinate. This means that the increase in density is relatively less in lower than in higher concentrations. This makes a new and important distinction between suspensoids and emulsoids which might well be studied experimentally in greater detail. The numerical values betray the curvature even more plainly than their graphic representation, for if the increases in density with unit increases in concentration are compared, it is found that the density increases uniformly with increasing con-

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[1] J. M. van Bemmelen, Gesam. Abhandl., 275, 458, Dresden, 1910.
[2] See the textbooks of physical chemistry for further details.
[3] S. E. Linder and H. Picton, Journ. Chem. Soc., **67**, 71 (1895).
[4] G. Quincke, Drude's Ann. d. Physik. **9**, 800 (1907); **10**, 486, 809 (1903).

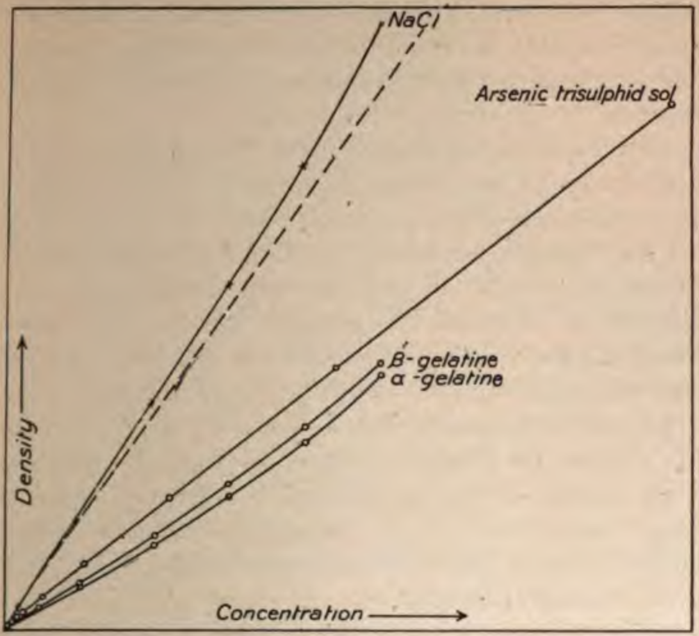

FIG. 20.—Relation of density to concentration in colloids.

TABLE 7.—CONCENTRATION-FUNCTION OF DENSITY IN COLLOID SOLUTIONS

<table>
<tr><th colspan="2">As_2S_3 sol (S. E. Linder and H. Picton)</th><th colspan="3">α-gelatine (G. Quincke)</th><th colspan="3">β-gelatine (G. Quincke)</th><th colspan="3">NaCl (Karsten[1])</th></tr>
<tr><th>Concentration, percent</th><th>Density</th><th>Concentration, percent</th><th>Density</th><th>Δ</th><th>Concentration, percent</th><th>Density</th><th>Δ</th><th>Concentration, percent</th><th>Density</th><th>Δ</th></tr>
<tr><td>0.0172</td><td>1.000137</td><td>5</td><td>1.014</td><td>28</td><td>5</td><td>1.014</td><td>30</td><td>1</td><td>1.0064</td><td>355</td></tr>
<tr><td>0.0344</td><td>1.000267</td><td>10</td><td>1.028</td><td>26</td><td>10</td><td>1.030</td><td>30</td><td>5</td><td>1.0355</td><td>371</td></tr>
<tr><td>0.0688</td><td>1.000535</td><td>20</td><td>1.054</td><td>34</td><td>20</td><td>1.060</td><td>34</td><td>10</td><td>1.0726</td><td>379</td></tr>
<tr><td>0.1375</td><td>1.001050</td><td>30</td><td>1.088</td><td>34</td><td>30</td><td>1.094</td><td>38</td><td>15</td><td>1.1105</td><td>392</td></tr>
<tr><td>0.2750</td><td>1.002110</td><td>40</td><td>1.122</td><td>44</td><td>40</td><td>1.132</td><td>40</td><td>20</td><td>1.1407</td><td>407</td></tr>
<tr><td>0.5500</td><td>1.004200</td><td>50</td><td>1.166</td><td></td><td>50</td><td>1.172</td><td></td><td>25</td><td>1.1904</td><td></td></tr>
<tr><td>1.1000</td><td>1.008435</td><td colspan="3" rowspan="3">Silicic acid (G. Quincke)</td><td colspan="3" rowspan="3">Tannin (aqueous) (G. Quincke)</td><td></td><td></td><td></td></tr>
<tr><td>2.2000</td><td>1.016080</td><td></td><td></td><td></td></tr>
<tr><td>4.4000</td><td>1.033810</td><td></td><td></td><td></td></tr>
<tr><td></td><td></td><td>1</td><td>1.1005</td><td>29</td><td>2.5</td><td>1.0101</td><td>200</td><td></td><td></td><td></td></tr>
<tr><td></td><td></td><td>3</td><td>1.017</td><td></td><td>5.0</td><td>1.0200</td><td>209</td><td></td><td></td><td></td></tr>
<tr><td></td><td></td><td>5</td><td>1.029</td><td>30</td><td>10.0</td><td>1.0409</td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td></td><td>10</td><td>1.059</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

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[1] From Landolt-Börnstein, Physik.-Chemisch. Tabellen, 3 Aufl., 322.

centration (see under Δ in the third column of Table 7). In future determinations of the density-concentration functions of colloids this sensitive mathematical proof should be given due preference.

It should also be emphasized that the density-concentration curve of molecular dispersoids, especially that of electrolytes, is concave toward the density axis (see NaCl in Table 7 and Fig. 20). This is already apparent from the fact that the contraction of volume on dilution of salt solutions, for example, is most pronounced in concentrated solutions and becomes less with increasing dilution. When a concentrated salt solution is diluted one-half and this dilution is again diluted one-half, etc., the observed contraction becomes progressively less. This corresponds to the two concave curves of Fig. 20. Here again there are evident interesting parallels between the properties of emulsoids and of molecularly dispersed solutions of salts, etc. Attention has been called to such similarities before and the occasion will arise again later.

The older measurements of W. Schmidt (*l.c.*) and Ch. Lüdeking (*l.c.*) were doubtlessly carried out with impure materials so that they cannot be considered here. Thus the density of a 20 percent solution of gelatine, according to Lüdeking, is 1.130 while according to Quincke it is only 1.054. This indicates, even if we make allowance for possible temperature differences, that Lüdeking used a gelatine much richer in salts than did Quincke. A measurement of the concentration-function when the salt content is known, would perhaps be interesting for the theory of the internal changes in state of gelatine, in other words, in a study of the influence which gelatine and dissolved salt have upon each other.

4. Thermal Coefficient of Expansion in Colloids.—Observations analogous to the above may be made on the thermal (cubic) coefficients of expansion in colloids. Here also we would anticipate the behavior to be analogous, roughly, to that of molecular dispersoids but the absolute changes in the constants of the pure dispersion medium in the case of colloids would not be expected to be as great as in the case of molecular dispersoids. We would also expect the emulsoids to bear a closer resemblance to molecularly and ionically-dispersed systems than the suspensoids.

In this connection it must be specially emphasized that the change in volume of pure water with increasing temperature above 40°C. is represented by a curve concave toward the temperature axis. In the case of a salt solution this curve is flatter, in fact it tends in high concentrations to approximate a straight line.[1] The form of the curve indicates that molecularly dispersed aqueous systems expand more at lower temperatures than water, and less than this at higher temperatures. There exists a region therefore in which the expasion coefficient of solution and of dispersion medium are the same. The curves for the solution and for the pure dispersion medium cross each other as shown diagrammatically in Fig. 21. For NaCl this temperature is about 55°. According to M. P. de Heen[2] the point of intersection depends upon the nature of the salt only, and not upon its concentration. It would be interesting to determine how colloid solutions behave in this respect.

From the meager material available the following figures of Rodewald are here reproduced, on the *average* thermal coefficient of expansion of starch with varying water content. The coefficient of expansion α is the ratio of volume increase to original volume. The temperatures employed range between 0° and 20°C.

TABLE 8.—THERMAL EXPANSION COEFFICIENT OF THE SYSTEM STARCH-WATER
(After Rodewald)

Water content of starch, percent	Thermal coefficient of expansion
0.00	0.000104
10.23	0.000167
10.19 ("air dry")	0.000236 0.000240
41.05 ("saturated" with H_2O)	0.000383

The calculated values and their graphic representation show that the thermal coefficient of expansion increases in linear ratio with the water content. It must be borne in mind that in starch we are not dealing with a typical colloid, but with a coarsely disperse system which assumes a typical colloid character only after becoming very rich in water.

Though we possess but few measurements on pure colloid solutions we have many experimental data on the thermal expansion of a *special* type of colloid system, namely, the gels of rubber and gelatine. But these exhibit complicated and special properties which can be discussed to advantage only after the general properties of gels have been described.

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[1] See Wilh. Ostwald, Lehrb. d. allg. Chem., 2 Aufl., 791, Leipzig, 1903.

[2] See Wilh. Ostwald, *l.c.*

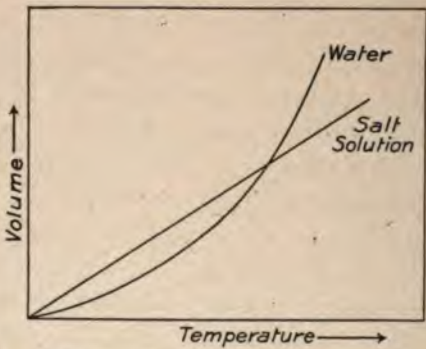

FIG. 21.—Diagram illustrating relation of changes in volume to changes in temperature in water and in salt solution.

§22. Vapor Tension, Boiling Point and Freezing Point of Colloid Solutions

1. General Remarks.—Among the most important physical changes which a liquid (or solid) dispersion medium suffers in taking up a molecularly or ionically dispersed phase, are the lowering of its vapor tension and its freezing point; and the elevation of its boiling point. The great importance of these phenomena resides in the simple quantitative relations which exist, according to the investigations of A. Wüllner, F. Raoult, and others, between the amount of these changes and the concentration of the molecularly dispersed phase. These relations, together with the laws of osmosis, have been combined by J. H. van't Hoff in his classic theory of true solutions. It might now be asked if colloids show a corresponding behavior. Investigations of this character were made long ago. The result may be expressed thus: *Pure colloids* (that is such as are as free as possible from molecular dispersoids) *affect only very slightly the vapor pressure, freezing point, and boiling point of the dispersing medium.* It even seems as if some colloids which can be obtained in a high state of purity do not influence these properties at all.

To the above statement must be added another more general and perhaps even more important one: *The amount of change in these properties, more particularly in the freezing point, in the vapor pressure and in the boiling point, depends upon the degree of dispersion of the system, and increases with every increase in the degree of dispersion.* A ready method by which a steady change in the degree of dispersion may be produced is to vary the relative amounts of dispersion medium and disperse phase. In support of this general statement may be cited the anomalous behavior of molecular dispersoids in concentrated solution commonly accounted for through association, polymerization, etc.; further, as previously mentioned,[1] "*concentration-variable dispersoids*" are by no means rare. To this important class of systems belong most of the emulsoids, as the chapters on "internal changes in state," "gelation," and "swelling" will clearly show. Thus F. Krafft[2] and A. Smits[3] found that *dilute* soap solutions showed quantitatively determinable elevations of the boiling point and depressions of the vapor pressure which became progressively less with increase in the concentration of the solution until they finally became zero. The measurements of A. Smits, upon which is based the law stated in the first part of this paragraph are reproduced in the following table:

TABLE 9.—AQUEOUS SOLUTIONS OF SODIUM PALMITATE

Molar concentration	Elevation of boiling point	Molar concentration	Reduction of vapor pressure
0.0282	0.024	0.50	1.3 mm. Hg.
0.1128	0,045	0.75	0.5
0.2941	0.050	1.00	0.0
0.5721	0.060		

It is especially interesting to note that though the elevation of the boiling point increases with increasing concentration, even though but little, the lowering of the vapor pressure decreases *absolutely* at higher concentrations. It is therefore evident that the two kinds of changes in no sense parallel each other, much less that a mathematical proportionality exists between them.

2. Measurements of Vapor Pressure of Colloid Solutions.—Other measurements of vapor pressure, besides those carried out

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[1] See p. 35.

[2] F. Krafft, Ber. d. Dtsch. Chem. Ges., **29**, 1328 (1896).

[3] A. Smits, Z. f. physik. Chem., **45**, 608 (1903).

[illegible] Richardson. [illegible] dispersion [illegible] impossible. [illegible] of the [illegible] those of [illegible]

[illegible] the [illegible] of the [illegible] disperse [illegible] vapor tension [illegible]

[illegible] measure- [illegible] These meas- [illegible] be compared [illegible] structures [illegible] They are [illegible] of the vapor [illegible] appear [illegible]

[illegible] Boiling Point [illegible] Solutions.—Boiling [illegible] solutions [illegible] and [illegible]

Picton,[1] A. Lottermoser,[2] F. Krafft (*l.c.*), A. Smits (*l.c.*), and many others. All the values obtained were exceedingly small, and became even smaller as the purity of the employed colloid solution increased. This applies both to emulsoids (gelatine, silicic acid, dextrine, rubber, starch, etc.), and to suspensoids (arsenious trisulphide hydrosol, mercuric sulphide hydrosol, stannic acid hydrosol, etc.).

4. Depression of Freezing Point of Colloid Solutions.—Because of the relative ease with which the experimental work of determining the freezing-point depression is carried out, such determinations have been made very frequently. Deserving of particular mention are those of H. T. Brown and G. H. Morris,[3] J. H. Gladstone and W. Hibbert,[4] A. Sabanejew,[5] E. Paternò,[6] N. Ljubavin,[7] A. Sabanejew and N. Alexandro,[8] S. E. Linder and H. Picton,[9] C. E. Linebarger,[10] G. Tammann,[11] W. Meyer,[12] St. Bugarsky and L. Liebermann,[13] H. Friedenthal,[14] F. Krafft,[15] A. Lottermoser,[16] N. Pappadà,[17] T. Körner and P. Düllberg,[18] Z. Gatin-Gruszewska,[19] W. R. Whitney and J. Blake,[20] G. Malfitano and Michel,[21] F. Bottazzi and G. D'Enrico,[22] T. B. Robertson and Th. C. Burnett,[23] J. Duclaux[24] and G. Moruzzi.[25] The results are entirely analogous to those obtained in determinations of the raising of the boiling point. One fact stands out clearly, however. Owing to the greater number of substances that have been investigated, colloid solutions have been found which show an undoubted depression of the freezing point. This is easily understood, if we bear in mind the variation which colloids show in their degree of dispersion.

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[1] S. E. Linder and H. Picton, Jour. Chem. Soc., **61,** 114 (1892).

[2] A. Lottermoser, Anorganische Kolloide, 74, Stuttgart, 1901.

[3] H. T. Brown and G. H. Morris, Journ. Chem. Soc., **53,** 610 (1888).

[4] J. H. Gladstone und W. Hibbert, Philos. Mag. (5), **28,** 38 (1889).

[5] A. Sabanejew, Journ. d. Russ. physik.-chem. Ges., **21,** 515 (1889) and **22,** 102 (1890); Ber. d. Dtsch. chem. Ges., **23,** 87 (1890); **24,** 558 (1891).

[6] E. Paternò, Z. f. physik. Chem., **4,** 457 (1889).

[7] N. Ljubavin, Journ. d. Russ. physik.-chem. Ges., **21,** 397 (1889).

[8] A. Sabanejew and N. Alexandrow, *ibid.*, **23,** 7 (1891).

[9] S. E. Linder and H. Picton, Journ. Chem. Soc., **61,** 114 (1892).

[10] C. E. Linebarger, Silliman's Am. Journ. (3), **43,** 416 (1892).

[11] G. Tammann, Zeitschr. f. physik. Chem., **20,** 180 (1896).

[12] W. Meyer, Zur Kenntnis einiger anorgan. Kolloidsubstanzen. Diss., Halberstadt (1897).

[13] St. Bugarsky and L. Liebermann, Pflüger's Arch. f. Physiol., **72,** 51 (1898); u. Tangl, *ibid.*, **72,** 531 (1898).

[14] H. Friedenthal, Physiol. Zentralbl., **12,** 849 (1899).

[15] F. Krafft, Ber. d. Dtsch. chem. Ges., **32,** 1614 (1899).

[16] A. Lottermoser, Anorganische Kolloide., **74,** Stuttgart, 1901.

[17] N. Pappadà, Gazz. Chim. Ital., **32** (II), 22 (1902); also G. Bruni and N. Pappadà (*l.c.*, 1901).

[18] T. Körner and P. Düllberg, Deutsche Gerberztg., **47** (1904).

[19] Z. Gatin-Gruszewska, Pflüger's Arch. f. Physiol., **102,** 569 (1904).

[20] W. R. Whitney and J. Blake, Journ. Amer. Chem. Soc., **26,** 1339 (1904).

[21] G. Malfitano and Michel, Compt. rend., **143,** 1141 (1907).

[22] F. Bottazzi and G. D'Enrico, Pflüger's Arch., **115,** 359 (1906).

[23] T. B. Robertson and Th. C. Burnett, Journ. Biol. Chem., **6,** 105 (1909).

[24] J. Duclaux, Compt. rend., **148,** 714 (1909).

[25] G. Moruzzi, Bioch. Zeitschr., **22,** 232 (1809).

An interesting study has been made by H. Friedenthal (*l.c.*) of the molecular weight of the so-called soluble starch. This starch may be prepared in various ways, among others by treating common starch with ozone. The product so obtained appears in every way to be "*depolymerized*," that is, to be more highly dispersed than ordinary starch. This is betrayed by the slight, but nevertheless definite depression of the freezing point exhibited by the soluble starch, in contrast to ordinary starch, as the following table shows.

TABLE 10.—DEPRESSION OF THE FREEZING POINT OF SOLUBLE STARCH
(According to H. Friedenthal)

Concentration, per cent.	Depression of the freezing point
2.5	0.005
5.0	0.01
10.0	0.02

There even exists a proportionality between concentration and freezing-point depression. The calculated molecular weight of soluble starch is about 9450, while, according to H. T. Brown and G. H. Morris (*l.c.*) that of normal starch is at least 32,400. These freezing-point measurements have also shown that the observed depressions of the freezing point have decreased as the solutions under investigation have been purified through dialysis, etc. Gatin-Gruszewska (*l.c.*) found solutions of very pure glycogen to show no depression of the freezing point whatsoever.

The relations existing between changes of vapor pressure, boiling point and freezing point of colloids, and their molecular weights will be discussed later.

§23. Mass-relations in Colloids

1. Concentration of Colloid Systems.—The *concentration* of a disperse system is expressed by the quantitative relation of t e disperse phase to the dispersing medium. But, while the properties of any "true" solution of a non-electrolyte are unambiguously defined by the concentration, this is by no means the case in coarser dispersoids, particularly in colloids.

In molecular dispersoids such as the "true" solutions of any non-electrolyte, we may assume that in a given dispersion medium the disperse phase will always have the same degree of dispersion; in other words, the disperse phase will always assume a state of maximum or molecular subdivision. This assumption is based upon the validity of the gas laws and Avogadro's hypothesis. The assumption no longer holds, of course, when we deal with electrolytes, or with molecular dispersoids of such concentration that a change in the degree of dispersion, such as "polymerization," etc., takes place; or when van't Hoff's laws are no longer strictly obeyed. And yet all these factors, which tend to make ambiguous the term "concentration" when applied to the proportionality existing between amount of molecular dispersoid and dispersing medium, are but slight in their effects when compared with the influence of the degree of dispersion upon the properties of the coarser dispersoids, particularly the colloids. For as has been repeatedly emphasized in the first chapters of this book, it is the specific surface which primarily gives to disperse systems their characterizing properties. The same relative proportion between the mass of dispersion medium and disperse phase may therefore exist in two disperse systems; in other words, they may have the same concentration, and yet in other respects show an entirely different behavior due to differences in degree of dispersion. A given amount of gold, for example, may, at one time, be distributed in a given amount of dispersing medium in the form of a coarse suspension, at another in the form of a gold-sol, in a third as an ionic dispersoid.[1]

To the above must be added, that many dispersoids, particularly colloids, are concentration-variable systems; that in other words, they often change their state when merely diluted with a given dispersion medium. This question will be handled in detail later. Variation with concentration appears to be the *rule* with emulsoids, as already indicated on p. 47. Such variations are not impossible, however, in suspensoids. Thus J. Reissig[1] found in his ultramicroscopic investigations, that the number of particles was not proportional to the content of colloid material, but that relatively *more* particles became visible in diluted solutions. While principles of optics have been marshalled to explain this behavior[2] it nevertheless appears possible that a division of the disperse phase into particles more highly disperse takes place, just as conversely the union of smaller particles to form larger aggregates on increase of concentration has been directly observed (see p. 88).

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[1] See The Svedberg, Koll.-Zeitschr., 4, 168 (1909).

It follows, therefore, that the definition of concentration in dispersoids which do not possess a maximum (molecular or ionic) degree of dispersion, will require an additional clause expressing the degree of dispersion of the disperse phase. Strictly speaking, all statements of the concentration of colloid systems ought to be given in some such manner as follows: Gold-hydrosol of x percent gold content and $x.10^y$ dispersion (or specific surface).

2. Experimental Work on Saturation in Colloid Solutions.—In dealing with molecular dispersoids we are in the habit of expecting to encounter a maximum ratio between dispersion medium and disperse phase, in other words, we expect to encounter a *saturation concentration*. Does such a saturation concentration exist in more coarsely disperse systems such as colloid systems?

Every investigator, who has concerned himself with the preparation of colloid solutions is familiar with the fact that pure, two-phase systems are frequently stable only within narrow limits of concentration. It is well known that suspensoids in particular can be prepared only in low concentrations, unless a third "protecting" phase is present. Although precise measurements are lacking, we find that most of the hydrosols described in the literature contain less than 0.5 percent of the metal by weight.

The maximum silver content of a silver sol, according to A. J. Prange[3] is 0.475 percent by weight; that of gold sols fluctuates, according to L. Vanino[4] between 0.0002 percent and 0.06 percent by weight; according J. Donau[1] it fluctuates between 0.0002 percent and 0.05 percent. R. Zsigmondy[2] thinks that 0.12 percent is the maximum concentration, and G. Bredig,[3] who prepared the gold sol by the electrical method regards 0.014 percent to be about the maximum. It appears, therefore, that the "saturation-concentration" for colloid gold lies between 0.1 and 0.2 per cent. Other metal hydrosols gave similarly low ranges of concentration. M. Traube-Mengarini and A. Scala[4] found that the spontaneous solution of lead in distilled water yielded a maximum content of colloid lead equal to 0.0069 percent after 42 hours; after 72 hours, 0.0078 percent, after 96 hours, 0.0092 percent, and after 3 months, 0.0089 percent. Ultimately, therefore, a constant lead content was obtained. But these values hold only when we deal with *pure* metal sols; when "protective colloids" are used the concentrations may rise much higher.

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[1] J. Reissig, Ultramikroskop. Beobacht. Diss., Erlangen, 1908. Review in Koll.-Zeitschr., **5**, 265 (1909).

[2] See the paper of Reissig and the paragraphs in this volume on ultramicroscopy.

[3] A. J. Prange, Rec. Trav. chim. Pays-Bas, **9**, 121 (1890).

[4] L. Vanino and co-workers, Koll.-Zeitschr., **2**, 272 (1907); **2**, 52 (1907).

The above statements agree in bringing out the fact that the metal content of metal hydrosols is always low. This statement could be further supported by additional references to the literature. In contrast herewith stand the results of P. J. Cholodny,[5] W. R. Whitney and J. Blake,[6] who obtained stable gold and silver sols of incomparably higher concentration. Thus P. J. Cholodny claims to have obtained pure silver sols containing more than 30 percent silver. This high concentration is so unusual that without making confirmatory investigations, one would be inclined to assume that it is due to an admixture of impurities, such as emulsoid silver, or iron hydroxide; or that one is dealing with a coarse suspension. Still more remarkable is the finding of Whitney and Blake who worked with red colloid gold prepared by the reduction of an ethereal gold chloride solution with acetylene gas.[7] By means of an electric current they concentrated this to a thick red "mud." According to the authors this "mud" when stirred up with distilled water again gave colloid solutions similar to the original but of high concentration. They managed in this way to obtain systems having a metal content of several percent. But here again the resulting solutions had, no doubt, but a low dispersion value, although the red color would in itself not warrant such a conclusion (see for example Table 2, p. 32). A repetition of these investigations with the aid of the ultramicroscope, which was not available when the above-named authors did their work, would certainly prove interesting.

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[1] J. Donau, Öst. Monatsh. f. Chem., **26**, 525 (1905).

[2] R. Zsigmondy, Liebigs Arm., **301**, 33 (1898).

[3] G. Bredig, Zeitschr. f. angew. Chem., 951 (1898).

[4] M. Traube-Mengarini and A. Scala, Koll.-Zeitschr., **6**, 249 (1910).

[5] P. J. Cholodny, Journ. russ. phys.-chem. Ges., **35**, 585 (1903); abstracted in Koll.-Zeitschr., **2**, 340 (1908).

[6] W. R. Whitney and J. Blake, Journ. Amer. Chem. Soc., **26**, 1339 (1904).

[7] J. Blake, Silliman' Am. Journ. Sci., **16**, 38 (1903).

Somewhat higher concentrations of colloids of a suspensoid character but not of metals have been observed, although, as a rule, such concentrated solutions are rather unstable, their colloid phase tending to precipitate in coarsely disperse form. S. E. Linder and H. Picton (*l.c.*) obtained a sol of arsenious sulphide containing 4.4 percent by weight of the disperse phase. Colloid sulphur with water as the dispersing medium may be prepared, according to M. Raffo,[1] containing up to 4.58 percent of sulphur. By farther improvements on Raffo's method Sven Odén[2] has obtained sulphur sols containing up to 50 percent of disperse phase.

In contrast to the suspensoids, the *typical* emulsoids exhibit no upper limit of concentration corresponding to a saturation concentration. Gelatine, silicic acid, or egg-albumin will, with proper regulation of the temperature, take up progressively greater or smaller amounts of water, without separating out in coarsely disperse form. The explanation of this behavior, which is so different from that of the suspensoids, is that the typical emulsiods represent *complex concentration-variable* systems, or, expressed more simply, mixtures of mutually soluble components.

Here again those systems that form transitions between suspensoids and emulsoids are particularly interesting. Thus, the hydroxides, especially the hydroxides of iron, seem to behave like suspensoids in dilute solution, and like emulsoids in concentrated solution (see §9). Because of this, fluid iron hydroxide sols may be obtained in concentrations characteristic of suspensoids (up to 4.8 percent according to G. Geffcken[3]); while on the other hand a jelly-like emulsoid modification of iron hydroxide is known, which contains but a few percent of water.[4]

3. Theoretical Considerations Bearing on the Saturation of Colloids.—In the older literature one frequently encounters the statement that colloid solutions differ from the molecularly disperse in lacking a saturation concentration. The above facts show that this is not borne out by experience, at least not as far as suspensoids are concerned. In recent years a number of investigators besides myself, namely, J. Duclaux,[1] W. M. Bayliss,[2] M. Traube-Mengarini, and A. Scala (*l.c.*) among others, have plainly expressed themselves in favor of a saturation concentration for colloids. The method employed to obtain the value of the critical concentration must be considered, whether this be by boiling down a dilute colloid solution, by allowing it to evaporate spontaneously, by removing the dispersing medium through filtration (L. Duclaux) or by determining the maximum spontaneous colloid solubility, say of lead (M. Traube-Mengarini and A. Scala, *l.c.*), or congo-red in water (W. M. Bayliss, *l.c.*), etc. The different methods do not yield the same values, as J. Duclaux (*l.c.*) has pointed out.

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[1] M. Raffo, Koll.-Zeitschr., **2**, 358 (1908).

[2] Sven Odén, Der kolloide Schwefel, Nov. Act. Reg. Soc. Sci. Upsaliensis (iv), **3**, 65 (1913).

[3] G. Geffcken, Zeitschr. f. physik. Chem., **49**, 299 (1904).

[4] See, for example, J. M. van Bemmelen, Die Absorption, Dresden, 1910.

While experimental evidence seems to indicate that for suspensoids there is an upper limit beyond which the system is not stable, a precise determination of it appears to be connected with serious difficulties. As already pointed out, the saturation concentration of molecular dispersoids varies with mere variations in the degree of dispersion of the material which is to be dissolved as shown, for example, by the increased solubility of a substance of moleculodisperse solubility, when a very finely ground powder is used. One may accordingly expect highly disperse colloids to have a higher saturation concentration than colloids of a lower degree of dispersion. A statement of where lies the saturation point in a colloid, just as a statement regarding the concentration of a colloid, would therefore be unambiguous only if the degree of dispersion of the colloid could be stated at the same time. In addition, however, this circumstance arises, that the disperse phase of most colloid systems contains particles of different dimensions. The instability which results from this will be discussed later. This constitutes a further complication in the definition of the saturation point of colloid systems.

It is interesting in this connection to bear in mind that *coarsely* disperse systems must also show a "saturation concentration."

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[1] J. Duclaux, Compt. rend., **148**, 295 (1909); Koll.-Zeitschr., **7**, 79 (1910).
[2] W. M. Bayliss, Koll.-Zeitschr., **6**, 25 (1910).

Such a critical concentration must appear the more sharply the more uniform the degree of dispersion of the disperse phase. The existence of such critical concentrations in coarse emulsions was first pointed out by Wa. Ostwald.[1] If we consider the disperse phase to consist of *rigid* spherical particles of equal diameter, the highest attainable concentration will be reached when the largest possible number of spheres are packed into a given space, in which case each sphere will be in contact with twelve others. The ratio: volume of disperse phase to volume of dispersion medium is then about 74: 26, or about 74 percent of disperse phase in the total volume of disperse system.

No such limit however arises when the disperse phase is liquid and therefore easily deformable; to fulfil the latter condition, it is also necessary that the interfacial tension between the phases, which resists deformation, should be low. In this case a futher increase in the percentage of disperse phase leads to flattening of the spheres at the points of contact until the droplets of disperse phase become polyhedra, the most probable forms being either rhombic dodecahedra or the fourteen-faced polyhedron with curved faces described by Lord Kelvin.

That these conditions are actually and not only theoretically possible is proved by the existence of very stable emulsions of petroleum in soap solution containing up to 99 percent of the former as disperse phase. Such emulsions have been prepared by S. U. Pickering[2] by special methods, while it is quite easy to make emulsions containing 90 percent of disperse phase, the droplets of which must be almost completely polyhedral.

These considerations become much more complicated when, as is generally the case, the particles are of different sizes. It is however obvious that this may lead to even more complete filling of a given space, so that the general conclusion remains correct, viz., that there is no upper limit of concentration when both phases are liquid. The behavior of emulsoids is therefore, in this respect also, in close agreement with the assumptions made throughout this work regarding their constitution.

4. Supersaturation in Colloid Systems.—We are familiar with the fact that even in molecular dispersoids our conception of saturation is a purely relative one. This is evidenced by the existence of phenomena of *supersaturation*. As is well known, a larger quantity of material yielding a molecularly disperse solution can be dissolved, if particles of more than molecular size are excluded, than when such is not the case. But, as Wilh. Ostwald[1] has shown, the quantity (and therefore the size) of the "nucleus" which is thus capable of suspending the state of supersaturation is by no means infinitely small—it is not even so small as to come within the range of molecular dimensions. The minimum quantity of sodium chlorate necessary to suspend the supersaturation of a molecular disperse solution of the same salt is equal to about 10^{-10} grams. Small as this quantity is, it nevertheless corresponds to a cube whose sides are several microns long, so that it is too large to fall even within the range of colloid dispersoids. Moleculo-disperse solutions could therefore contain particles of more than molecular dimensions without suspending the state of supersaturation[2] and the proportion of the two phases to each other, in other words, the saturation concentration could vary greatly depending upon the part played by the non-molecular phase. That such mixed, stable systems exist is evidenced by the fact that at high concentrations many molecular dispersoids assume the properties of colloid systems. Thus C. A. Lobry de Bruyn and L. H. Wolff[3] have shown that highly concentrated cane-sugar solutions show the Tyndall phenomenon. It seems not impossible that an "enlargement of the molecules" or polymerization takes place in high concentrations of all molecular dispersoids, only the particles rarely attain colloid dimensions. Our definition of concentration and saturation in all such systems requires an additional clause expressing the dispersion of the system.

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[1] Wa. Ostwald, Koll.-Zeitschr., **6**, 105 (1910); see also M. W. Beyernick, *ibid.*, **7**, 16 (1910); Wa. Ostwald, *ibid.*, **7**, 64; (1910) E. Hatschek, *ibid.*, **7**, 111 (1910).

[2] S. U. Pickering, Koll.-Zeitschr., **7**, 11 (1910).

But there exists in colloid systems also an interesting series of phenomena which can be satisfactorily explained only if we assume the possibility of supersaturation in them. Thus solutions of gold may be prepared from which colloid gold separates spontaneously in high concentrations, but in which this does not occur or only after prolonged standing, if the solution is more dilute. R.

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[1] Wilh. Ostwald, Zeitschr. f. physik. Chem., **22**, 289 (1897).

[2] See also in this connection the numerous papers by P. P. von Weimarn in the Kolloid-Zeitschrift and the Kolloid-chemische Beihefte.

[3] C. A. Lobry de Bruyn und L. H. Wolff, Rec. trav. chim. des Pays. Bas., **23**, 155 (1904).

Zsigmondy,[1] L. Vanino and F. Hartl,[2] The Svedberg,[3] Fr. Doerinckel[4] and others have shown that the formation of colloid gold in such mixtures may be accelerated by adding a few drops of a previously prepared second solution of colloid gold. According to Zsigmondy silver sols may be prepared by thus "inoculating" silver solutions with colloid particles. Similar supersaturation phenomena occur in the silver sols of the photographic plate, according to Lüppo-Cramer.[5] It is of great interest that such phenomena are encountered among emulsoids. Thus H. Garrett[6] found that gelatine solutions congeal more rapidly if some solid gelatine prepared by rapid cooling of the same solution is added to them. F. Eduardoff[7] has noted that the natural emulsions of rubber from certain rubber plants, which undergo "spontaneous" coagulation when exposed to the air, coagulate more rapidly if a piece of solid (*i.e.*, already coagulated) rubber is introduced into the liquid. Eduardoff believes that he has excluded the possibilities of a chemical action in this illustration. The experiments of W. Biltz and A. von Vegesack[8] should also be cited here. They found that in emulsoid night-blue hydrosol the increase in viscosity due to ageing is accelerated by "inoculation" with small amounts of already viscid night-blue (for details see §25).

The view that all these phenomena are due to the suspending of a state of supersaturation, which gives rise to coarsely disperse systems can hardly be doubted.

§24. Molecular Weight of Substances in the Colloid State as Measured by Changes in the Constants of the Dispersing Medium

1. General Remarks.—The quantitative relations which exist between concentration and the lowering of the vapor pressure, the elevation of the boiling point, or the depression of the freezing point of molecularly disperse solutions, allow of the determination of molecular weight. Such determinations must evidently become more difficult and less reliable as the amount of such change becomes smaller. As shown in §22 these changes almost disappear in dispersoids of medium or low dispersion, such as the colloids. A source of great error in these investigations is the molecularly dispersed impurities present in such colloids which can be removed only with greatest difficulty. Experiments have been made on the effect of concentration of the colloid upon the lowering of the freezing point and the elevation of the boiling point of the dispersing medium and no change has been noted.

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[1] R. Zsigmondy, Z. f. physik. Chem., **56**, 65, 57 (1906).
[2] L. Vanino and F. Hartl, Ber. d. Dtsch. chem. Ges., **39**, 1699 (1906).
[3] The Svedberg, Koll.-Zeitschr., **6**, 238 (1910).
[4] Fr. Doerinckel, Z. f. anorg. Chem., **63**, 344 (1909).
[5] Lüppo-Cramer, Koll.-Zeitschr., **7**, 99 (1910).
[6] H. Garrett, Über d. Viskosität einiger Kolloid-Lösungen usw. Diss. Heidelberg, 1903; Philos. Mag. [6], **6**, 374 (1903).
[7] F. Eduardoff, Gummi-Zig., **23**, 809 (1909).
[8] W. Biltz and A. von Vegesack, Z. f. physik. Chem., **73**, 509 (1910).

To this must be added that in the cases in which a change in freezing point, boiling point, etc., with change in concentration of colloid has been observed, the amount of such change has not been even approximately proportional to the change in concentration, as the previously cited investigations of G. Tammann and D. Konowalow show. The recent investigations of T. B. Robertson and Th. Burnett[1] of the freezing point of casein in the presence of m/30 KOH show that this remains constant, even when the casein content of the solution varies to the extent of 50 percent. In colloid solutions not even the *sense* may be preserved of the relations between concentration and changes in these properties. Thus, as shown on p. 130, the elevation of the boiling point instead of increasing may decrease relatively, or even absolutely, in soap solutions with increase in concentration. The changes in state which are responsible for this behavior are not limited to this example, but doubtlessly occur in solutions of egg-albumin when the relative proportions of disperse phase and dispersing medium are changed. Finally, it should be emphasized that it is possible to prepare systems having the same chemical composition but of progressively varying degrees of dispersion (see for example p. 143). In view of these facts a discussion of the "molecular weights of colloid substances" loses all significance. Otherwise an investigation of the aqueous arsenious trisulphide solutions of Linder and Picton, would show a series of progressively varying "molecular weights" for one and the same chemical substance in the same solvent, which in the coarser suspensions would approach infinity. The interest attached to a quantitative or graphic determination of the relations between "molecular weights" and the size of the particles, for a general theory of the dispersoid state, scarcely requires emphasis.

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[1] T. B. Robertson and Th. Burnett, Jour. Biol. Chem., 6, 105 (1909).

It follows from the above that one cannot properly speak of the molecular weights of dispersoids having a colloid or lower degree of dispersion as one does of the molecular weights of molecular dispersoids as deduced from changes in the constants of their solvents. Measurements of the vapor pressure, the boiling point and the freezing point of colloid systems certainly do not justify it. This needs to be emphasized, for only recently have investigators like S. Arrhenius,[1] T. B. Robertson, etc., based *chemical* conclusions upon the "molecular weights" of such colloid systems as egg-albumin without paying attention to the variability in degree of dispersion with changes in concentration. It cannot be emphasized too strongly that not even the direction of the changes in solution constants with changes in concentration need be the same in the case of colloids, as shown by the soap solutions referred to on p. 129; much less does there exist a proportionality between such changes and concentration as the laws of van't Hoff demand. For the same reason the mass law of chemical reactions[2] is not applicable to colloid systems, for (in its ordinary form) this assumes a proportionality between molecular concentration and concentration by weight.

2. Examples of the "Molecular Weights" of Substances in the Colloid State as determined by Changes in the Constants of the Dispersing Medium.—Even though the value of determining the "molecular weight" of colloid substances is a rather doubtful one after what we have said, we shall nevertheless give a few examples as determined from changes in vapor pressure, boiling point and freezing point.

Of older determinations may be mentioned those of J. H. Gladstone and W. Hibbert[3] who found that purified egg-albumin shows an unmeasurably slight depression of the freezing point. The same authors found caramel to show a molecular weight of 1585 to 1745; gum arabic, one of 1612 to 2001; rubber in benzene, one of 6504. Later measurements by the same method, carried out by St. Burgarsky and L. Liebermann (*l.c.*), gave for egg-albumin a molecular weight of 6400, for albumose, 2400, for pepsin, 760. Sabanejew and Alexandrow (*l.c.*) find egg-albumin to have a molecular weight of 14270. From freezing-point determinations T. B. Robertson and Th. Burnett (*l.c.*) assign a molecular weight of 1400 to 2000 to casein in the presence of bases. Z. Gatin-Gruszewska (*l.c.*) finds highly purified glycogen to have a "moleculr weight" of 140,000 or more.

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[1] S. Arrhenius: Immunochemie, 16, 19, 24, etc., Leipzig, 1907.

[2] See in this connection the textbooks of physical chemistry; for example, Wilh. Ostwald, Grundr. d. allg. Chem. 4 Aufl., 341, 375, etc., Leipzig, 1909.

[3] For literature see pp. 130 and 131.

Of measurements of the boiling point of colloid systems those of F. Krafft and his pupils (*l.c.*) deserve special mention. The following table shows a particularly interesting series of their experiments. It shows at the same time that in the lower members of a homologous series the observed molecular weights in aqueous solution are at first lower than calculated, while the reverse is true with the higher members. We deal, in other words, with a series of dispersoids which vary in the degrees of their dispersion. Dispersion values characteristic of colloids begin, approximately, with nonylate.

TABLE 11.—MOLECULAR WEIGHTS OF AQUEOUS SODIUM-SOAP SOLUTIONS (Determined by Boiling-point Measurements.) After F. Krafft and A. Strutz[1]

Sodium salt	Concentration in percent	Molecular weight	
		Observed	Calculated
Acetate, $C_2H_3O_2$	0.9	50.5	82
	25.2	40.3	
Propionate, $C_3H_5O_2$	3.8	51.7	96
	19.8	42.6	
Caproate, $C_6H_{11}O_2$	3.5	72.8	138
	20.6	77.9	
Nonylate, $C_9H_{17}O_2$	3.4	144.1	180
	20.4	285.5	
Laureate, $C_{12}H_{23}O_2$	3.3	474.0	222
	16.1	507.0	
Palmitate, $C_{16}H_{31}O_2$	16.4	about 1060	278
	25.0	approaches ∞	
Stearate, $C_{18}H_{35}O_2$	about 16.0	about 1500	306
	27.0	approaches ∞	
(Oleate, $C_{18}H_{33}O_2$)	27.0		304
	26.5	approaches ∞	

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[1] F. Krafft und A. Strutz, Ber. d. Dtsch. chem. Ges., **29**, 1329 (1896).

Of "molecular weight determinations" in colloid systems obtained by measuring the vapor pressure those of H. Rodewald (*l.c.*) must be mentioned. From study of a starch-water system containing 68.37 percent of starch by weight Rodewald calculated this to have the unexpectedly low molecular weight of 4370.

It must be emphasized that a great number of observations of an entirely negative character stand out against the figures given above, and that it has been found generally true, as in the observations of Z. Gatin-Gruszewska (*l.c.*), that the molecular weights become progressively greater with increase in the purity of the colloid employed. It has been maintained by some authors (see, for example, T. B. Robertson, *l.c.*) that such purification, say of an aqueous colloid, is fundamentally wrong because the impurities represent *integral* parts of the colloid phase and should therefore be counted in with it as part of its "chemical constitution." It must, of course, be admitted that proteins, such as casein for example, can form salt-like compounds with electrolytes, though it is questionable whether we are in such cases really dealing with stoichiometrical relations or only "adsorption compounds." Salts of protein, especially salt-like compounds of the products of protein cleavage, do undoubtedly show measurable molecular weights (see p. 132); but that fact does not yet do away with the question of the "molecuar weight" of *pure* proteins, as these observers apparently fail to see. That electrolytes *need* not form an integral part of colloid systems is shown by the example of glycogen cited above and by such compounds as metastyrol[1] which also causes no measurable rise in boiling point. The "explanation" of these facts as given by these authors, according to which there occurs a great "polymerization" of the protein when pure, resulting in an abnormal molecular weight is only a restatement in chemical terms of the physical fact that the degree of dispersion of a pure protein solution has assumed the values characteristic of colloid systems.

Parenthetically, it is well to point out even here that similarly high values have been found when the "molecular weights" have been determined by other means. It must be acknowledged that there exist considerable discrepancies between the values obtained by the methods here discussed and by the "dynamic" methods of determining the molecular weight (as by direct measurement of the osmotic pressure, diffusion velocity, etc.). Protein solutions, for example, exhibit a *direct* osmotic pressure, while they show no measurable rise in the boiling point.[1] Even these facts are sufficient to show that a careless application of van't Hoff's laws of solution is not to be made to colloid systems, for the necessary quantitative relationships are lacking. For this reason it seems better to return to mere description of the individual groups of phenomena observed in colloid systems and so obtain laws by inductive methods which will, perhaps, be analogous to, but not identical with, those of "true" solutions.

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[1] G. Posnjak, Das Metastyrol usw., 15, Diss., Leipzig, 1910.

II. INTERNAL FRICTION AND SURFACE TENSION OF COLLOIDS

§25. Internal Friction of Colloid Systems

1. General Remarks.—The internal friction or viscosity of colloids has not yet been as thoroughly investigated as the viscosity of molecular dispersoids. Yet this very property demands special study in the case of colloids. Even slight changes in colloids, particularly in the case of the emulsoids, so greatly affect this value that even Thomas Graham justly called the viscosimeter a "colloidoscope." Such viscosity measurements can, moreover, be easily made.[2] It is therefore rather strange that the attention of colloid investigators has only recently been directed to this problem.

The following are the main characteristics of *molecular* dispersoids:

When a solid goes into solution the viscosity of the dispersing medium is usually increased. Dilute solutions of some salts, such as lithium chloride and potassium chloride, form exceptions to this rule. These represent cases of so-called negative viscosity.

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[1] See, for example, R. S. Lillie, Amer. Jour. Physiol., **20,** 127 (1907). Another coarse discrepancy was pointed out above in discussing the behavior of soap solutions.

[2] The simplest apparatus and one yielding accurate results is the viscosimeter of Wilhelm Ostwald consisting of a U-shaped tube in which is measured the time of outflow of a constant volume through a capillary For details regarding the method see Ostwald-Luther-Drucker, Handbuch f. Physik.-chem. Messungen., **3,** 230, Leipzig, 1910.

When solid napthaline is dissolved at room temperature in alcohol a decrease in viscosity is also observed, according to experiments of my own. We here apparently deal with iso-dispersoid solvents which are "depolymerized" when the given substances are dissolved in them. In normal cases the viscosity increases progressively with concentration, but more rapidly than the latter, so that the viscosity-concentration curve is convex toward the concentration axis.

Manifold and complicated conditions arise when two *liquids* are molecularly dissolved in each other. Thus, the mixture of alcohol with water shows a characteristic behavior in that a maximum of viscosity is obtained in medium concentrations of the one in the other, the value of which is considerably greater than that of the pure components. For further details the reader must be referred elsewhere.[1] As already evident, this behavior corresponds closely with the extremely variable viscosity observed in emulsoids.

When gases are dissolved in a solvent they do not seem to change its viscosity.[2]

2. Internal Friction of Suspensoids.—It may be regarded as typical of suspensoids that *their viscosity is but slightly greater than that of their pure dispersing media.* It must be remembered, however, that this is true only when such systems are dilute (see p. 135). In concentrated form the mass of the disperse solid phase may predominate over that of the dispersing medium, as when powders are merely moistened, so as to be coated by a thin but continuous liquid membrane. Such systems may be so viscid that their properties approximate those of solids. We need but recall how moist sand may be cut into slices, and the rigidity of the scales and crusts of dried colloid metals. From this it follows that with increase in concentration the viscosity of a suspensoid rises very slowly at first, but very suddenly and greatly in high concentrations.

Most viscosity measurements of suspensoids have been made on dilute preparations as by J. Friedländer,[3] F. Bottazzi and

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[1] A recent review with original experiments is found in the dissertation of R. Kassel, Viskosität binärer Flüssigkeitsgemische, Leipzig, 1910.

[2] At least no changes were observed with the ordinary gases (O, N, CO_2, CH_4). See Wo. Ostwald and A. Genthe, Zool. Jahrb., Abth. f. Biol., **18**, 12 (1903).

[3] J. Friedländer, Zeitschr. f. physik. Chem., **38**, 430 (1901).

G. d'Errico,[1] on glycogen solutions, and by H. W. Woudstra[2] and others on silver hydrosols. Measurements carried out on transition systems such as iron hydroxide sols will be discussed below. In needs to be emphasized that glycogen solutions are typical suspensoids only in low concentrations, and that they assume an emulsoid character in higher ones. This is already evidenced by the fact that glycogen sols may be prepared which contain 26 to 45 percent of glycogen.[3] Nevertheless in low concentrations glycogen behaves as a typical suspensoid, and so its discussion seems appropriate in this place.

The viscosity of suspensoids appears to have been measured for the first time by J. Friedländer (*l.c.*) who could scarcely detect a difference between them and their pure dispersion media. For a suspension of rosin (10 cc. of a 1 percent alcoholic solution squirted into 150 cc. of water) he obtained a viscosity of 598.4; after 43 hours it had assumed a viscosity of 599.3. Pure water has a value of 599.6. A "very turbid" silver sol (Ag-Credé) gave 453.4 while pure water gave 452.3. These differences are scarcely greater than the experimental error. Even though these measurements refer to very dilute systems, they suffice to show how very slight are the changes in the viscosity of a liquid when it takes up a suspensoid phase.

More detailed work was then done by F. Bottazzi and G. d'Errico (*l.c.*) as well as by H. W. Woudstra (*l.c.*). Their more important results are given in Table 12 and in Fig. 22, to which have been added some data on sodium chloride obtained by A. Genthe and myself.

The curves and tables show that at certain concentrations there is a very sudden increase in viscosity. For silver and glycogen hydrosols these concentrations are respectively about 3.5 and 30 percent. The almost rectilinear character of the first part of the curves shows that for low concentrations the increase in viscosity is almost directly proportional to the colloid content. When these curves are compared with that for NaCl (0 to 25.52 percent), one notes a straighter curve. The uniformity of the

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[1] F. Bottazzi and G. d'Errico, Pflüger's Arch. f. Physiol., **115**, 359 (1906).

[2] H. W. Woudstra, Z. f. physik. Chem. **63**, 619 (1908); Chem Weekblad, **5**, 303 (1908); van Bemmelen-Gedenkboek, 36 (1910).

[3] According to Z. Gatin-Gruszewska, Pflüger's Arch., **102**, 569 (1904) only 20 percent solutions of *pure* glycogen can be prepared; if the glycogen contains salt its solubility is much greater.

TABLE 12.—VISCOSITY OF SUSPENSOIDS

Silver hydrosol (according to H. W. Woudstra). Temp. 26°		*Glycogen hydrosol* (according to F. Bottazzi and G. d'Errico). Temp. 37°			NaCl (for comparison), (according to Wo. Ostwald and A. Genthe).[1] Temp. 20°		
Concentration percent	Viscosity	Concentration percent	Viscosity (time of outflow), in sec.		Concentration percent	Viscosity sec.	
0.0000	1.0000	0	124	33	0	56.2	4.0
0.9310	1.0013	1	129		1	56.58	
1.9025	1.1021	5	157		10	60.21	
2.887	1.0045	10	208	51	15	65.95	5.8
3.369	1.0057	15	259	51	20	75.24	9.2
3.850	1.0098	20	440	191	25	87.44	12.2
4.904	1.0457	25	564*	124(?)	26.52	103.63	16.2
		30	914	350		110.7	
		35	1516	602			
		40	3549	2033			
		45	7688	4139			

* A second viscosimeter was used from this point on, the outflow time of which compared with the first as 1 : 2.6. All the values have been recalculated in terms of the first.

NaCl curve is still greater at higher temperatures, so that at a temperature corresponding to that at which the measurements on the colloids were carried out it would approximate a straight line.

The very slight absolute increase in viscosity at low colloid concentrations should be emphasized. Silver hydrosol containing 3.85 percent colloid silver is less than 1 percent more viscous than pure water, while a 5 percent solution of NaCl shows an increase of 6.6 percent. Glycogen shows a greater absolute increase in viscosity (about 4 percent for a 1 percent glycogen content). Still, molecular dispersoids are also known which yield such high figures, as in the case of sugar in water. Furthermore, as already mentioned, glycogen solutions are not to be regarded as typical suspensoids.

So far as the relation is concerned of the sudden increase in viscosity here noted to the critical concentrations previously discussed, it may be said that the behavior of silver hydrosol at the 3.5 percent concentration coincides with the *first* of these critical regions. It is interesting, and incidentally confirms the idea that dilute glycogen solutions have a suspensoid character, that F. Bottazzi and G. d'Errico (*l.c.*) also emphasize the slightness of increase in viscosity that can be observed. On the scale chosen for Fig. 22 this increase is scarcely apparent. The figures of Table 12 shows clearly, however, a decided increase between the concentrations of 15 to 20 percent. The steepening of the curve in Fig. 22 at 45 percent indicates that at this point the suspensoid character of the system is possibly beginning to make way for a more emulsoid one.

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[1] Wo. Ostwald and A. Genthe, Zool Jahrb., Abt. f. Biol., **18,** 1 (1903).

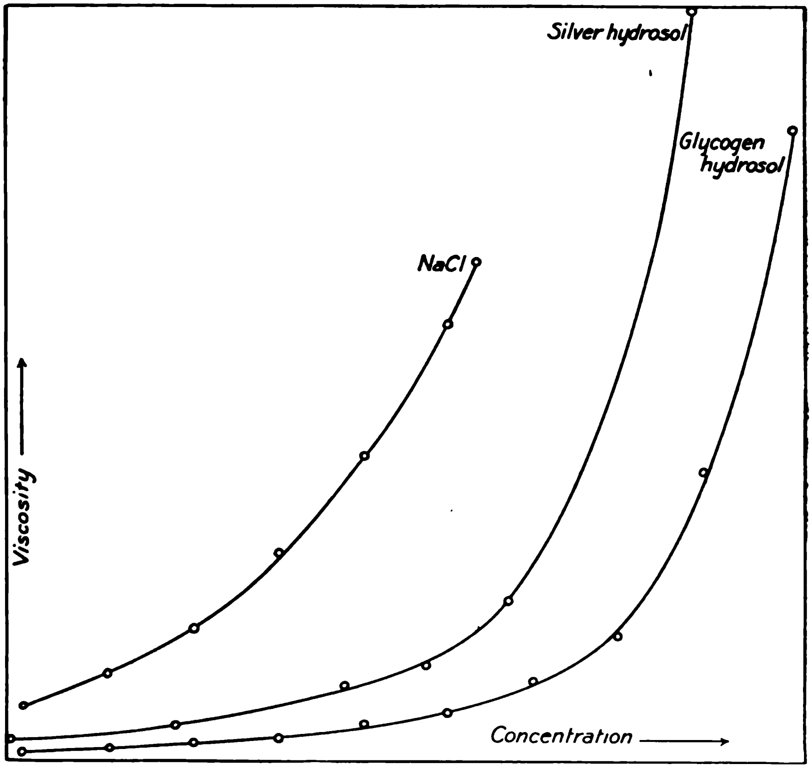

FIG. 22.—Viscosity of suspensoids. (According to *H. W. Woudstra, F. Botazzi* and *G. d'Errico.*) The curve for NaCl has been added for purposes of comparison.

Of special interest is a series of viscosity measurements carried out by Sven Odén[1] on sulphur sols. These sols, which the author obtains by a modification of Raffo's method, are remarkable both for the unusually high concentrations which may be reached, and for the limits within which the degree of dispersion can be varied. The viscosity-concentration curves for two extreme cases are shown in Fig. 23, the lower curve being that for a sol consisting of particles 0.1μ diameter, while the upper one represents the viscosity of a sol consisting of microscopic particles estimated at 0.01μ diameter.

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[1] Sven Odén, Zeitschr. f. physik. Chem., 80, 709, 1912.

It will be noticed that the latter curve lies entirely above the former, in other words, for any given concentration the viscosity of the more highly dispersed sol is higher than that of the less dispersed one. The deviation from the linear ratio is also more marked in the former than in the latter, especially at higher concentrations. These results are unambiguous, while the attempts already described to alter the degree of dispersion by coagulants, etc., lead to results which are capable of more than one interpretation.

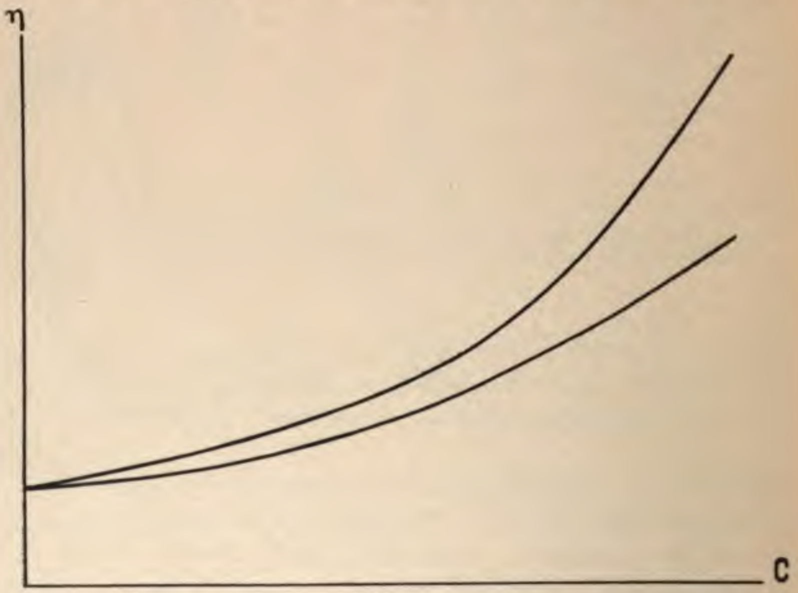

FIG. 23.

3. Effects of External Conditions upon Viscosity of Suspensoids.—*Temperature* affects the viscosity of suspensoids in the same way as it does that of normal liquids: the viscosity decreases with increasing temperature. There is nothing especially peculiar about the viscosity of suspensoids when compared with that of molecular dispersoids or that of pure dispersion media. The fact, however, that the viscosity of suspensoids is *thermostable*, in other words, that it is the same for a given temperature whether one starts from a higher or a lower one is very important. The previous thermal history does not influence the viscosity of suspensoid colloids any more than it does that of molecular dispersoids. This is indicated by the experiments of F. Bottazzi and G. d'Errico (*l.c.*) on glycogen solutions as reproduced in the following table.

TABLE 13.—INFLUENCE OF THERMAL HISTORY ON VISCOSITY OF A 10 PERCENT SOLUTION OF GLYCOGEN

(According to F. Bottazzi and G. d'Errico)

Temperature	Time of outflow in seconds after		
	Heating	Cooling	Δ
70°	120	123	−3
60	137	143	−6
50	157	164	−7
40	189	191	−2
30	234	233	+1
20	284	286	−2

Although the deviations all tend toward the same side they scarcely exceed the limits of experimental error, particularly if one considers that the slightly greater values may have been due to evaporation, for the measurements on the cooled solutions were made later than those on the warmed solutions.

This behavior of the suspensoids stands in marked contrast to that of the emulsoids as will appear below. The suspensoids tend here to behave like the molecular dispersoids which is rather unusual, for ordinarily the emulsoids do this.

According to H. W. Woudstra (*l.c.*) the *addition of electrolytes* influences the viscosity of a suspensoid silver hydrosol (and probably that of all suspensoids) in a very characteristic manner. The addition of an electrolyte decreases the viscosity. To judge from the behavior of molecular dispersoids one would expect an increase in viscosity upon adding an electrolyte but actually the opposite occurs. It should be noted, however, that this decrease takes time, occurring in some instances only after days, and that it is associated with a change in the state of the colloid, namely, with its coagulation. The following table shows this behavior.

TABLE 14.—INFLUENCE OF ELECTROLYTES ON THE VISCOSITY OF SILVER HYDROSOL

(According to H. W. Woudstra)

28 cc. silversol + 1 cc. K_2SO_4 solution = 0.015 millimol.

Time in days	Viscosity
After 4 days	1.0507
After 18 days	1.0126
After 34 days	1.0047
After 36 days*	1.0088(?)
After 47 days*	1.0043

* The asterisk signifies that silver has begun to precipitate.

The *influence of age* on the viscosity of a suspensoid is closely connected with the above. H. W. Woudstra (*l.c.*) found that silver sols gradually become less viscous even when nothing is added to them. This is explained by the fact that in the preparation of most inorganic colloids small quantities of electrolytes are retained by the colloids, and these tend to bring about coagulation. Table 15 may serve as an example.

TABLE 15.—INFLUENCE OF AGE ON THE VISCOSITY OF A SILVER HYDROSOL

(According to H. W. Woudstra)

Age in days	Viscosity
3	1.0457
17	1.0201
28½	1.0107
37	1.0077
52*	1.0118(?)

* Silver has begun to precipitate; the higher viscosity value may perhaps be explained by clogging of the capillary.

We must keep in mind that the action of electrolytes and of age in decreasing the viscosity of suspensoids is the direct opposite of their effect on the viscosity of most emulsoids, as will be discussed below.

4. Mechanical Theory of the Viscosity Relations in Suspensoids.—A mathematical theory of the viscosity of suspensions was first formulated by A. Einstein[1] incidentally in a paper on another subject. The formula which he deduces for a suspension of small, rigid and—in proportion to their radius—widely separated spheres is:

$$\eta' = \eta(1 + 2.5f)$$

where η is the viscosity of the dispersion medium, η' that of the suspension, and f the ratio $\frac{\text{aggregate volume of solid}}{\text{total volume}}$.

The radius of the spheres does not appear and the viscosity is accordingly independent of their size, in other words the degree of dispersion, and increases in linear ratio with the concentration.

A formula which is functionally identical with Einstein's but has the proportionality factor 4.5 instead of 2.5 was deduced independently by E. Hatschek[2] in 1910. His method of doing so has been criticised adversely by M. von Smoluchowski.

It is obvious from the viscosity-concentration curves already given that the formula holds good only to a very limited extent, since the increase in viscosity is much more than linear in most instances, and since, for a given concentration, the viscosity is greater for a higher degree of dispersion. The reasons for this discrepancy are several: for one thing, the distance between particles is certainly small in concentrated suspensions and suspensoids; for another, as M. von Smoluchowski (*l.c.*) points out, Einstein's result is obtained by neglecting all but the first term of a Taylor's series, the second of which already contains a power of the radius. The best agreement with the formula was obtained by M. Bancelin,[3] who tested it on suspensions of gamboge particles of different diameters made according to Perrin's method. He found the viscosity to be independent of the degree of dispersion and to increase in linear ratio with the concentration up to 3 percent, with a proportionality factor of 2.9 instead of the theoretical 2.5.

E. Hatschek[4] has suggested as possible explanations of both deviations from the Einstein formula that 1) the more than linear increase shown in most series of measurements may be due to errors caused by the use of the capillary viscosimeter, and 2) the higher viscosity of highly dispersed suspensions may be caused by the adsorption layer on the particles. If this were of the same thickness for all sizes of particles (of the same substance), it would of course increase the volume of a given mass of small particles much more than that of an equal mass of large ones. He shows that an absorption layer of only 0.87 $\mu\mu$ thickness would account for the difference exhibited by Sven Odén's two sulphur sols (see above). M. von Smoluchowski (*l.c.*) considers both suggestions tenable.

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[1] A. Einstein, Ann. d. Phys., **19**, 289 (1906).
[2] E. Hatschek, Koll.-Zeitschr., **7**, 301 (1910).
[3] M. Bancelin, Koll.-Zeitschr., **9**, 154 (1910).
[4] E. Hatschek, Koll.-Zeitschr., **11**, 280 (1912).

To eliminate the possible errors due to the capillary viscosimeter, E. Humphrey and E. Hatschek[1] carried out a series of measurements in a modification of the apparatus employed by Couette and other observers. This consists of a hollow clyinder, closed at the bottom and capable of being rotated round its axis, and a second cylinder of somewhat smaller diameter suspended coaxially in the former and provided with a mirror for measuring the deflection from the position of rest. The space between the cylinders is filled with the liquid under examination. If the outer cylinder is now rotated at uniform speed, the suspended one is deflected by an angle which, other things being equal, is proportional to the product: angular velocity × viscosity (suitable precautions being taken to eliminate the effects of the flat ends, etc.) In addition to being free from the possible defects of the capillary instrument, the apparatus offers the important advantage that the viscosity can be measured over a wide range of low and arbitrarily chosen rates of shear, while in the capillary instrument each measurement is carried out at a different, and, in general, at a very high rate of shear.

Humphrey and Hatschek investigated a suspension of sifted rice starch grains (3μ average diameter) in a mixture of carbon tetrachloride and toluene having the same specific gravity, in concentrations of 2, 4 and 6 percent. They found that the viscosity, for any given concentration, *varied with the rate of shear, being highest at the lowest rate of shear.* The difference becomes more marked at higher concentrations. At any one rate of shear the increase in viscosity is more than linear with concentration.

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[1] E. Humphrey and E. Hatschek, Proc. Physical Soc., Lond., **28**, Pt. V, 274 (1916).

As the viscosity of a suspension is thus a function of two variables —concentration and rate of shear—the complete relation must be represented by a surface, a portion of which is represented in parallel projection in Fig. 24. The sections nearly parallel with the plane of the paper show viscosity at definite concentrations as a function of the rate of shear; those at right angles, viscosity at definite rates of shear as a function of the concentration. The whole behavior is evidently very complicated and in urgent need of further investigation, both theoretical and experimental.

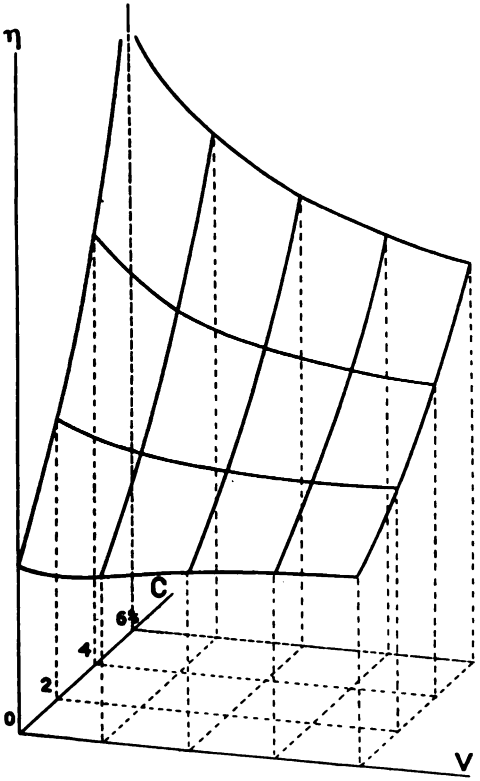

FIG. 24.

5. Viscosity of Emulsoids (Literature).—A comparison of the viscosity of emulsoids and coarser emulsions with that of suspensoids has recently been the object of thorough study. From the great literature on this subject we may mention the papers of P. von Schroeder[1] (gelatine), V. Henri, Lalou, A. Mayer, Stodel,[2] H. Garrett[3] (silicates, gelatine, albumin), A. Müller[4] (organic colloids), E. Lacqueur and O. Sackur[5] (casein), Du Pré Denning[6] (iron hydroxide), W. B. Hardy[7] (globulin, etc.), G. Fano, G. Rossi, O. Scarpa, J. Simon[8] (albumin, gum arabic, iron hydroxide, etc.), S. Axelrod[9] (rubber), S. J. Levites[10] (gelatine, agar, etc.), W. Flemming[11] (silicates), Wo. Pauli[12] and co-workers (albumin, etc.), Gokun[13] (gelatine), W. Frei[14] (gelatine), V. Albanese[15] (albumin, etc.), P. Schidrowitz and Goldsbrough[16] (rubber), G. Moruzzi[17] (acid albumin), F. Galdi[18] (theory), H. Handovsky[19] (albumin), W. Biltz[20] and co-workers (organic dyes), L. Michaelis and B. Mostynski[21] (albumin), F. Bottazzi and C. Victorow[22] (soaps), N. Sahlbom[23] (iron hydroxide sol), W. E. Ringer[24] (acid albumin), H. Chick and C. J. Martin (casein),[25] H.

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[1] P. von Schroeder. Z. f. physik. Chem., **45**, 75 (1903).

[2] V. Henri, Lalou, A. Mayer, Stodel, Compt. rend. Soc. de Biologie, **55**, 1668 (1903).

[3] H. Garrett, Diss. Heidelberg, 1903; Phil. Mag. (6), **6**, 374 (1903).

[4] A. Müller, Ber. d. Dtsch. chem. Ges., **37**, 11 (1903, 1904).

[5] E. Laqueur und O. Sackur, Hofmeisters Beitr., **3**, 193 (1903).

[6] Du Pré Denning, Diss. Heidelberg, 1904.

[7] W. B. Hardy, Journ. Physiol., **33**, 251 (1905); Proc. Roy. Soc. B., **79**, 413 (1907).

[8] G. Fano und G. Rossi, Arch. di Fisiol., **1**, 492, 609 (1904) (rubber, starch, serum); G. Rossi, *ibid.*, **2**, 500 (1905); with O. Scarpa, *ibid.*, **2**, 246 (1905) (iron hydroxide); G. Rossi, *ibid.*, **2**, 272, 599 (1905) (albumin); E. Cavazzani, *ibid.*, **2**, 513 (1905) (milk); G. Rossi, *ibid.*, **3**, 171, 507 (1906) (contains a review of the literature up to 1906); J. Simon, *ibid.*, **4**, 594 (1907); **5**, 394, 402, 470, 477, 479 (1908) (albumin + alcohol), etc.

[9] S. Axelrod, Gummizeitung, **19**, 1053 (1905); **20**, 105 (1905); **23**, 810 (1909). For earlier experiments see C. O. Weber, Chemistry of India-rubber, 80, London, 1902.

[10] S. J. Levites, Koll.-Zeitschr., **2**, 210 (1907).

[11] W. Flemming, Z. f. physik. Chem., **41**, 407 (1907).

[12] Wo. Pauli (in part with H. Handovsky, K. Schorr, R. Wagner, Samec, etc.) Hofmeisters Beitr., **11**, 415 (1908); Koll.-Zeitschr., **3**, 2 (1908); Kolloidch. Studien am. Eiweiss, Dresden, 1908; Biochem. Zeitschr., **27**, 296 (1910); Sitz. Ak. Wiss. Wien, 17 März, 1910; 30 Juni, 1910; Koll.-Zeitschr., **7**, 241 (1910).

[13] Gokun, Koll.-Zeitschr., **3**, 84 (1908).

[14] W. Frei, Transvaal Med. Journ., Aug., 1908.

[15] V. Albanese, Arch. ital. Biol. **50**, 387 (1909).

[16] P. Schidrowitz und Goldsbrough, Journ. Soc. Chem. Ind., **28**, 3 (1909); Koll.-Zeitschr., **4**, 226 (1909).

[17] G. Moruzzi, Bioch. Zeitschr., **22**, 232 (1909).

[18] F. Galdi, Il Tammazi, **3**, Nr. 5; Gior. Ind. Sc. Med. 1909; Rivist. di chem. et micr. clinic., **9**, 1909.

[19] H. Handovsky, Bioch. Zeitschr., **25**, 510 (1910); Koll.-Zeitschr., **7**, 183, 267 (1910).

[20] W. Biltz (with A. von Vegesack, Steiner, etc.) Z. f. physik. Chem., **73**, 500 (1910).

[21] L. Michaelis and B. Mostynski, Bioch. Zeitschr., **25**, 401 (1910).

[22] F. Bottazzi and C. Victorow, Rend. R. Ac. Linc., **19**, 659 (1910).

[23] N. Sahlbom, Koll.-chem. Beih., **2**, 79 (1910).

[24] W. E. Ringer: van Bemmelen-Gedenkboek, 243 (1910); this volume contains a rich literature.

[25] H. Chick and C. J. Martin, Koll.-Zeitschr., **11**, 102 (1912).

Chick (serum proteins),[1] F. Baker (very complete data on nitrocellulose in various solvents),[2] R. Gaunt (india rubber),[3] F. Kirchof (india rubber).[4]

Valuable results have been obtained, of which only the more important can be pointed out here.

6. Viscosity Changes in Emulsoids with Time.—In experiments on the viscosity of emulsoid solutions the investigator is most impressed by the great changes in viscosity observable in one and the same colloid with time. To be sure the behavior of suspensoids indicated that these too suffer viscosity changes, but the variations occur more slowly. "Spontaneous" changes in viscosity in pure suspensoids are usually to be reckoned in *days* (see p. 152), whereas in typical emulsoids they often occur from *minute to minute*. Another very interesting difference (which may possibly serve to differentiate suspension from emulsion colloids) is the fact that the viscosity of emulsoid solutions usually *increases* with time, whereas that of suspensoids *decreases*.

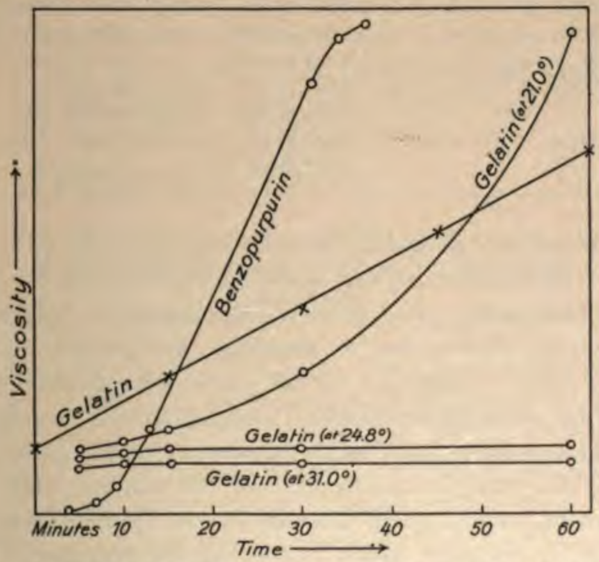

FIG. 25.—Increase in viscosity of emulsoids with time. (According to the experiments of *P. von Schroeder*, *S. J. Levites* and *W. Biltz*.)

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[1] H. Chick, Biochem. Journ., **8**, 261 (1914).

[2] F. Baker, Journ. Chem. Soc., **108**, 1653 (1913).

[3] R. Gaunt, Journ. Soc. Chem. Ind., **33**, No. 9 (1914).

[4] F. Kirchof, Koll.-Zeitschr., **15**, 30 (1914).

Table 16 and Fig. 25 give a picture of these changes.

Table 16.—Increase in Viscosity of Emulsoids with Time
(After P. von Schroeder, S. J. Levites, and W. Biltz)

Gelatine solution (P. von Schroeder) viscosity				**Gelatine solution** (S. J. Levites) viscosity		**Benzopurpurin** (W. Biltz) 0.4 per cent. (25°) viscosity	
Time	At 21.0°	At 24.8°	At 31.0°	Time	At 25°	Time	Time of outflow, seconds
After 5 min.	1.83	1.65	1.41	After 15 min.	2.19	After 4 min.	75.4
After 10 min.	2.10	1.69	1.41	After 30 min.	2.39	After 7 min.	75.8
After 15 min.	2.45	1.74	1.42	After 45 min.	2.59	After 9 min.	77.0
After 30 min.	4.13	1.80	1.42	After 60 min.	2.80	After 13 min.	81.2
After 60 min.	13.76	1.90	1.42	After 75 min.	3.00	After 31 min.	106.0
				After 90 min.	3.20	After 34 min.	109.0
				After 11 hr. gelatinized.	3.40	After 37 min.	110.2

The usual way in which viscosity changes with time is probably best represented by the S-shaped curve found by W. Biltz and A. von Vegesack (*l.c.*) in their experiments on benzopurpurin solutions. In other words, on standing, the viscosity of an emulsoid first rises. This part of the curve corresponds with the first portion of the curves obtained for gelatine by P. von Schroeder (*l.c.*). Then follows an almost *uniform* increase in viscosity as shown by the straight middle part of the curve. This straight line was also found by S. J. Levites (*l.c.*). Finally, there follows a *decrease* in viscosity which is represented graphically by the turn of the curve toward the abscissa. This late behavior is found not only in the case of benzopurpurin but also (slightly marked) in the gelatine curve of P. von Schroeder at 24.8°. The progressive variations in the viscosity observed under different experimental conditions and discussed below can all be interpreted theoretically in the terms of this S curve.

As shown by the experiments of P. von Schroeder (*l.c.*) on gelatine, the changes in viscosity with time decrease absolutely as well as relatively with rise in temperature. It is also an important fact that the changes with time are the more distinct the more concentrated the solution. Under certain conditions *dilute* emulsoids behave like molecular solutions, that is, they show a constant or perhaps a decreasing viscosity (see below, p. 160).

Thus, W. Biltz and H. Steiner (*l.c.*) could observe well marked changes in state in night-blue solutions at 50° only if they contained more than 3 percent of the dye. The effect of the addition of various substances, especially salts, upon the time-variations in viscosity was studied by Gokun (*l.c.*), who found that when small amounts (of ammonium nitrate) were added, the viscosity of gelatine solutions increased *more quickly* than without such, while if larger amounts were added (say 0.32 to 1.4 normal NH_4NO_3) the viscosity remained almost *constant*. In very high concentrations (5.6 to 6.4 normal NH_4NO_3) the viscosity *decreased with time* as in the case of suspensoids. The latter is doubtless due to the fact that in such high concentrations "precipitation effects," in other words, coagulatory effects begin to manifest themselves. The following table gives some illustrative figures which are, however, not very exact.

TABLE 17.—EFFECT OF THE ADDITION OF NH_4NO_3 ON THE CHANGE IN VISCOSITY OF A GELATINE SOLUTION (0.28 PERCENT) WITH TIME

(After Gokun)

Time	Concentration of the added salt in normality										
	0	0.175	0.35	0.7	1.05	1.4	2.1	2.8	3.5	4.2	5.6
After 44 hours	1.36	1.77	1,15	1.09	1.07	1.05	1.05	1.05	1.07	1.13	1.30
After 44 hours	1.42	1.80	1.70	1.41	1.35	1.12	1.05	1.05	1.06	1.08	1.18
After 67 hours	1.62	1.05(?)	1.77	1.54	1.32	1.15	1.07	1.01	1.0	1.08	1.18
After 91 hours	1.77	1.90	1,82	1.50(?)	1.32	1.17	1.07	1.05	1.08	1,08	1.15
After 115 hours	2.02	2.06	1.81	1.77	1.37	1.17	1.05	1.01	1.02	1.07	1,14

For the influence of non-electrolytes the reader is referred to the experiments of J. Simon (*l.c.*, 1907–08) on the effect of *alcohol* on the increase of viscosity with time in albumin solutions. This author found that the viscosity increased as he added *more* alcohol. Acetone had a similar influence while the higher alcohols were less effective. Fig. 26 gives a picture of the results.

A case differing from those hitherto mentioned in that it concerns an emulsoid which *spontaneously* grows *less viscous* with time has been described by H. W. Woudstra[1] in his work on the toluene sols of rubber. As he has made only a preliminary statement we cannot be sure that this case is a true exception. Woudstra found his carbon tetrachloride sols to become cloudy with time.[1] It seems possible, therefore, that under the experimental conditions chosen by this investigator his solutions coagulated, in which case their behavior would naturally be irregular. The method of *preparation* (swelling, trituration, filtration through glass wool) may also have influenced his findings. His solutions may have contained "undissolved" particles which at first caused a high viscosity, but which, later, after their "solution," led to decrease in the viscosity. Further experiments are needed on this point.

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[1] H. W. Woudstra: Kolloid-Zeitschrift, **5**, 33 (1909).

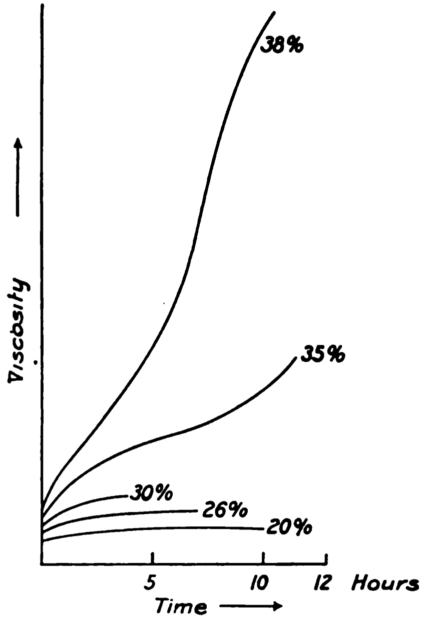

FIG. 26.—Effect of time upon the viscosity of serum albumin to which alcohol has been added. (According to *J. Simon*.)

In accord with Woudstra's observations are those of K. Schorr and H. Handovsky (*l.c.*, 1910) who found that albumin solutions first show a gradual increase in viscosity but later a slow decrease on the addition of *alkali*. Chemical changes (hydrolytic cleavage, etc.) which produce secondarily a decrease in viscosity, somewhat analogous to the hydrolytic action of ferments, are undoubtedly active here (see p. 164).

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[1] Dr. Brauer of Leipzig has also observed that filtered solutions of purified rubber which are originally entirely clear show flocculi after standing some weeks. Since then I have been able to make analogous observations on benzene rubber sols.

7. Effect of Mechanical Treatment of Viscosity of Emulsoids.—It is a remarkable fact that the viscosity of emulsoids is affected by mechanical treatment. If they are shaken for a period or simply pressed several times through a capillary, as in a viscosimeter, their viscosity *decreases*. Such phenomena have been observed by Gokun (*l.c.*) and W. Biltz (*l.c.*). They show that even in such apparently perfect liquids there is present a kind of "structure" which is destroyed by mechanical treatment. This structure seems closely allied with the oft-mentioned liquid membranes of the dispersion medium which surround the disperse particles. One may imagine that in higher concentrations these membranes unite, somewhat as represented in Fig. 14 in p. 87, and that mechanical treatment pulls the individual envelopes apart again. In favor of this view is the fact that, according to W. Biltz and H. Steiner, this phenomenon is particularly marked in concentrated solutions; and that the viscosities of solutions of different ages may be reduced to the same value by sufficient shaking (see Table 18).[1]

TABLE 18.—INFLUENCE OF SHAKING ON THE VISCOSITY OF A 2.7 PER CENT. SOLUTION OF NIGHT-BLUE

(According to W. Biltz and H. Steiner)

Without Shaking	After Shaking	
	a	b
151.5	118.2	117.0
143.4	118.0	117.0
139.9	118.4	117.4

8. Influence of "Inoculation" on Internal Friction of Emulsoids.—A remarkable phenomenon has been observed by H. Garrett (*l.c.*) in solutions of gelatine and by W. Biltz and H. Steiner (*l.c.*) in solutions of night-blue. They found their spontaneous increases in viscosity to be markedly accelerated through the addition of small quantities of aged or gelatinized solutions.

As the table shows, this behavior is best observed only in colloid solutions of high concentration.

It should be emphasized, as P. von Schroeder (*l.c.*) has shown, that this phenomenon depends upon a chemical change in the

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[1] In passing it may be mentioned that H. Zangger observed ordinary milk to show this behavior.

TABLE 19.—INFLUENCE OF INOCULATION ON THE INTERNAL FRICTION OF A SOLUTION OF TECHNICAL NIGHT-BLUE AT 25°

(According to Biltz and Steiner)

	Time of outflow							
	Without Inoculation			After Inoculation				
Per cent.	At once	After 1 day	After 6 days	At once	After ½ hr.	After 1 hr.	After 2 hr.	After 1 day
0.90	77.2″	78.5″	78.5″	79.2″	......	......	......	78.8″
1.35	79.3	82.0	81.6	82.2	......	......	......	82.0″
1.80	77.6	85.6	......	83.2	85.2	86.1	85.6	85.9
2.25	85.2	91.3	102.6	88.9	88.9	91.6	103.3	......

gelatine, probably upon its hydrolytic cleavage. This is proved not only by the fact that the decrease in viscosity, with prolonged heating, is irreversible, but also by the fact that it follows the laws of chemical mass action. Furthermore, after prolonged heating, precipitates appear in the solution, which I hold to be the products of this chemical reaction.[1] Analogous considerations apply to the changes in viscosity which silicic acid, etc., show when heated or otherwise treated (W. Flemming, *l.c.*). This view also supported by the fact that long heating decreases the viscosity of many emulsoids, though by no means all. W. Biltz and H. Steiner (*l.c.*), for example, found that emulsoids of night-blue do not alter their viscosity even after being heated 7 hours.

What has been said under headings 3 to 8 must always be borne in mind when making viscosity determinations on emulsoids. For this reason the discussion entered into here needed to precede a consideration of the relations between internal friction, concentration, temperature, etc.

9. Rate of Shear and Viscosity of Emulsoids.—As in the case of suspensions (Humphrey and Hatschek[2]) but in a much more marked degree, the viscosity of emulsoids is a function of the rate of shear. This could already be concluded from the experiments on gelatine sols by H. Garrett[3] in which the viscosity was measured by the oscillating disc method. The results are, however, not easy to interpret, since the rate of shear varies in every experiment from zero at the center of the disc to a maximum at its periphery. Measurements carried out by E. Hatschek[1] with the Couette apparatus already described do not suffer from these complications, and two curves thus obtained, in which again the rate of shear is plotted as abscissa and the viscosity as ordinate are shown in Fig. 27. Both curves were obtained with the same (0.5 percent gelatine) sol, the lower when the sol was 24 hours, and the upper (double one) when it was 72 hours old. The lower curve shows that the viscosity decreases with increasing rate of shear, although the difference is not very great. With the aged sol the viscosity is much higher throughout (see p. 154) and in addition the dependence on the rate of shear is extremely marked, the viscosity at the highest rate of shear being less than one-half of that measured at the lowest.

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[1] Wo. Ostwald, Pflüger's Arch., **109**, 277 (1905).

[2] E. Humphrey and E. Hatschek, Proc. Physical Soc. Lond., **28**, Pt. V, 274 (1916).

[3] H. Garrett, Diss. Heidelberg, 1903; Phil. Mag. (6), **6**, 374 (1903).

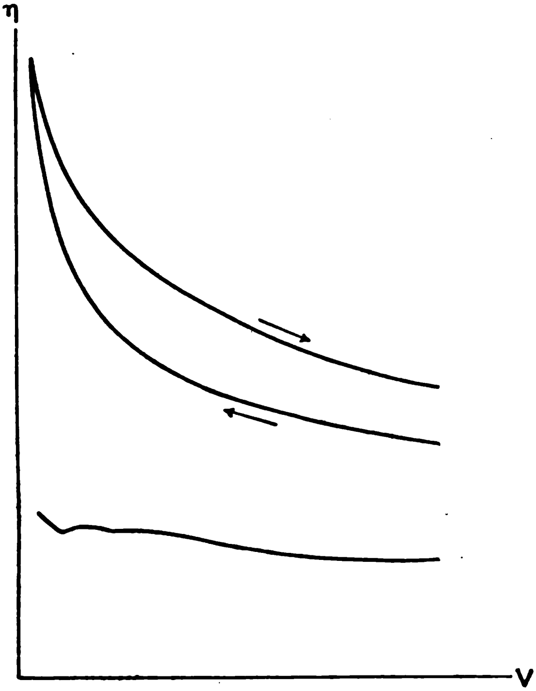

FIG. 27.

To make sure that this variation is really a function of the rate of shear, and not due to a permanent destruction of structure, the series of measurements on the aged sol was repeated in the opposite sense, *i.e.*, with increasing velocities. Marked hysteresis is shown, since the curve thus obtained lies entirely above the one found with decreasing velocities, but this shows conclusively that no permanent alteration in the system has taken place.

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[1] E. Hatschek, Koll.-Zeitschr., 13, 88, 1913.

10. Influence of Thermal History on Viscosity of Emulsoids.—When such typical emulsoids as gelatine, agar-agar, etc., are subjected to the influence of heat their viscosity is affected in the same way and as markedly as when they are treated mechanically. Prolonged heating decreases the internal friction of these solutions. By prolonged boiling, it is possible so to change a solution of gelatine or glue that it will no longer solidify when cooled. When alcohol is added to a gelatine solution thus altered by prolonged boiling, a yellow precipitate is thrown down, which is easily soluble in water. A precipitate similarly produced in normal gelatine only "swells" when thrown into cold water. This was observed as early as 1867 by Moritz Traube.[1] Traube called the modification which would no longer gelatinize, β gelatine or β glue in contrast to the normal, gelatinizing α form. Table 20 and Fig. 28 copied from P. von Schroeder (*l.c.*) illustrate what has been said. S. J. Levites[2] has made further experiments on

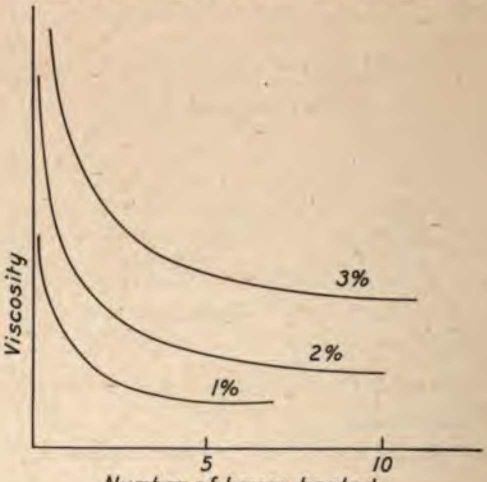

FIG. 28.—Effect of prolonged heating on the viscosity of a gelatine solution. (According to *P. von Schroeder*.)

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[1] M. Traube, Reichert und Du Bois Reymond's Arch., 87 (1867).

[2] S. J. Levites, Koll.-Zeitschr., 2, 239 (1907).

TABLE 20.—INFLUENCE OF HEATING ON THE VISCOSITY OF GELATINE SOLUTIONS
(According to P. von Schroeder)

Hours of heating to about 100°	Internal friction of gelatine		
	1 per cent.	2 per cent.	3 per cent.
0.5	1.29	1.75	....
1.0	1.23	1.55	....
1.5	1.20	1.49	....
2.0	1.17	1.47	1.76
2.5	1.15	....	....
3.0	1.14	1.37	1.68
3.5	1.13	....	....
4.0	1.13	1.32	1.56
4.5	1.11	....	....
5.0	....	1.30	1.54
5.5	1.11	....	....
6.0	....	1.28	1.50
7.0	....	1.26	1.47
8.0	....	1.25	1.47
9.0	....	....	1.44
10.0	....	1.24	1.42
12.0	....	1.23	1.40
14.0	....	1.22	1.39
16.0	....	1.22	1.39

purified gelatine (gluten), agar-agar and on the sodium salt of thymonucleic acid with entirely analogous results.

11. Influence of Concentration on Internal Friction of Emulsoids.—The influence of concentration upon the viscosity of

TABLE 21.—INFLUENCE OF CONCENTRATION ON VISCOSITY OF GELATINE SOLUTIONS
(According to S. J. Levites)

a Gelatine, at 35°		*a* Gelatine, at 35°	
Per cent.	Viscosity	Per cent.	Viscosity
0.25	1.10	0.5	1.186
0.5	1.22	1.0	1.262
0.75	1.32	1.5	1.332
1.0	1.46	2.0	1.432
1.5	1.75	3.0	1.603
2.0	2.05	4.0	1.856
3.0	2.96		

emulsoids simulates its effect upon suspensoids. This is clearly evident on comparing Figs. 29 and 22, in doing which it is well to limit oneself to comparisons involving the same temperatures. Examples of the effects of concentration are given in Tables 21 and 22.

Emphasis should be laid on the fact that the above measurements refer either to low colloid concentrations or were obtained at higher temperatures. As every one who has experimented with gelatine or agar-agar well knows, there is, for every typical emulsoid, an optimum concentration and an optimum temperature at which the solution gelatinizes. Thus solutions of night-blue above 1.575 percent are so thick at 0° that they no longer flow through a viscosimeter. We wish here merely to point out that the influence of concentration on viscosity in typical emulsoids is very great. Thus the viscosity of an agar-agar solution (at room temperature) varies within the first 2 percent from that of pure water to that of a solid. If one compares molar instead of percentage concentrations, the great absolute increases in the value as well as the abruptness of the viscosity changes appear still more striking.

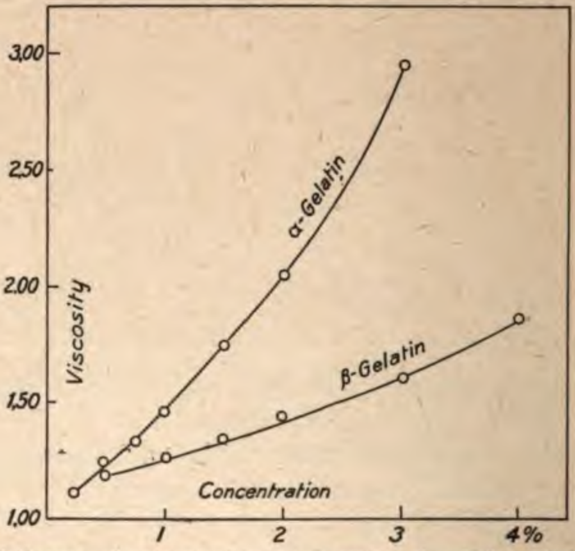

FIG. 29.—Influence of concentration on viscosity of gelatine solutions at 35°. (According to *S. J. Levites*.)

The effect of temperature on the concentration influence is such that decreasing the temperature makes the ascent of the curve steeper, while increasing the temperature flattens it (see Fig. 30). This behavior is analogous to that observed in molecular dispersoids and probably to that observed in suspensoids. Added substances like salts increase or decrease the slope of the curve as do temperature changes. Purification of the technical night-blue

TABLE 22.—INFLUENCE OF CONCENTRATION ON VISCOSITY OF NIGHT-BLUE SOLUTIONS

(According to W. Biltz and H. Steiner)

Technical night-blue						Purified night-blue	
At 50°		At 25°		At 0°		At 25°	
Concentration, percent	Internal friction	Concentration, percent	Internal friction after 6 days	Concentration, percent	Internal friction	Concentration, percent	Internal friction
0.225	1.007	0.025	0.985	0.225	1.009	0.25	1.008
0.45	1.019	0.045	0.990	0.45	1.026	0.50	1.027
0.675	1.027	0.090	0.994	0.675	1.042	0.75	1.058
0.90	1.041	0.145	0.997	0.90	1.068	1.00	1.068
1.125	1.054	0.180	0.996	1.125	1.101	1.25	1.091
1.35	1.071	0.225	1.006	1.35	1.132	1.50	1.106
1.575	1.090	0.270	1.006	1.575	1.176	1.75	1.145
1.80	1.097	0.315	1.006	1.80	1.180	2.00	1.171
2.025	1.125	0.360	1.008			2.25	1.221
2.25	1.141	0.405	1.014			2.50	1.263
2.475	1.157	0.450	1.019			2.75	1.334
2.70	1.178	0.495	1.020			3.00	1.403
3.15	1.240	0.540	1.033				
3.60	1.298	0.6075	1.037				
4.05	1.393	0.675	1.042				
4.50	1.455	0.7875	1.054				
		0.900	1.022				
		1.0125	1.065				
		1.125	1.080				
		1.237	1.110				
		1.35	1.105				
		1.575	1.139				
		1.80	1.182				
		2.025	1.272				
		2.25	1.390				
		2.475	1.480				
		2.70	1.525				

(which is ordinarily contaminated by about 43 percent sodium sulphate) decreases the slope of the curve, that is, has the same effect as raising the temperature. It is not impossible, however, that the addition of other salts, such as the chlorides, nitrates, etc., might have an opposite effect. Chemical changes in the colloid itself also change the character of the concentration curve, as is evident in the tables and curves referring to α and β gelatine.

12. Influence of Temperature on Viscosity of Emulsoids.—Besides the influence of concentration on the viscosity of emulsoids, described in the previous paragraphs, there exists also a relation between temperature and viscosity which is observed when all other factors are kept constant. But systematic investigations of this type over a larger temperature range have not as yet been made. For reasons already given, only dilute emulsoids can be used for such study. Some approximate determinations of the *average temperature coefficients* of the viscosity of emulsoids are, however, at hand. Thus the internal friction of pure water changes about 18 percent between 21° and 31°C. In contrast

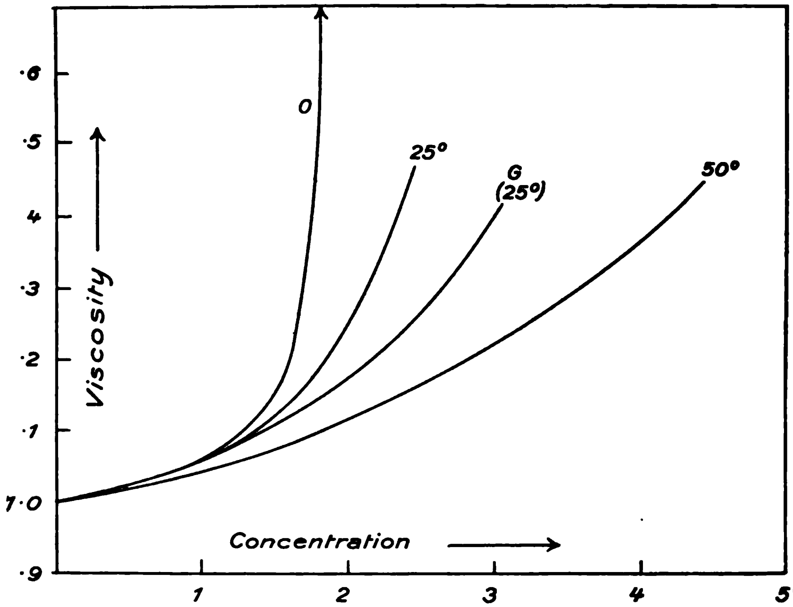

FIG. 30.—Influence of concentration on the viscosity of night-blue solutions. (According to *W. Biltz* and *H. Steiner*.) The curve marked "G" shows the behavior of the purified night-blue.

to this, the viscosity of a 3 percent gelatine solution, within the same temperature range, changes from 1.42 to 13.76, in other words, almost 1000 percent (P. von Schroeder, *l.c.*). According to Biltz and Steiner (*l.c.*), the absolute viscosity of a 1.8 percent solution of night-blue rises from 10.5 to 32 between 25° and 0°, in other words, triples, while the viscosity of water merely doubles under the same conditions. With higher concentrations the changes in viscosity within very narrow ranges of temperature become extraordinary, for the existence of gelatination and melting points means nothing else but that, within a temperature change of a degree or less, the viscosity of such systems changes from that of a fluid to that of a solid.

13. Influence of Added Substances on Viscosity of Emulsoids.—The influence of added substances on viscosity, when all other external factors have been kept constant, has also been thoroughly investigated. Of the mass of facts available in this field we shall mention only a few. For details the original papers should be consulted.

So far as the important effect of salts upon emulsoids is concerned, the accuracy of most of the earlier measurements is vitiated because impure preparations, contaminated with electrolytes, were used. Only recently have Wo. Pauli and his co-workers (*l.c.*), in a careful and searching series of investigations, shown what minute amounts of electrolytes suffice to cause substantial changes in the viscosity of organic emulsoids. Nevertheless older experiments with commercial preparations and those purified by ordinary laboratory methods are not valueless, for such colloids are used in many of the arts and for some scientific purposes.

We must distinguish between the effects of salts on the viscosity of emulsoids which with time are stable and those which are unstable. When of the latter class, as with gelatine, a distinction must be made between the initial value of the viscosity as observed immediately after the addition of a salt and the final value which is approached only asymptotically. According to the experiments of P. von Schroeder (*l.c.*), S. J. Levites (*l.c.*) and Gokun *l.c.*), the first of these values follows the general rule of mixtures: salts which raise the internal friction of water affect colloid solutions similarly, and *vice versa*. The final value exhibited by gelatine solutions after the addition of salts is very different from this

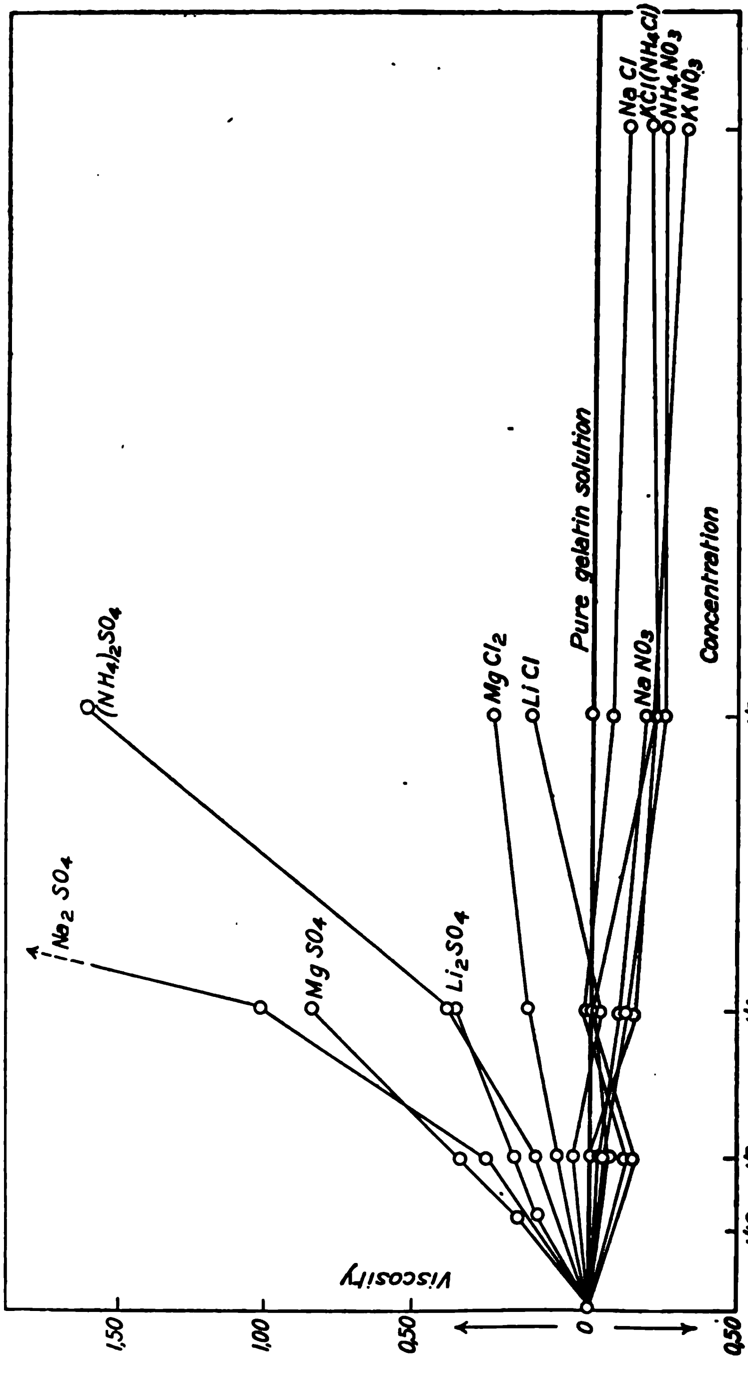

FIG. 31.—Effect of added substances upon the viscosity of gelatine solutions. (According to the experiments of P. von Schroeder.)

first. In Table 23 and Fig. 31, taken from P. von Schroeder (*l c.*), are collected a series of such viscosity values in gelatine solutions

TABLE 23.—A. INFLUENCE OF SALTS ON INTERNAL FRICTION OF GELATINE (After standing 1 hour)

Salt	Concentration		
	⅛ norm.	½ norm.	¼ norm.
Pure gelat.	1.78	1.73	1.78
Na_2SO_4	2.11....	2.72	9.41
K_2SO_4	1.97....	—	—
$(NH_4)_2SO_4$	1.95....	2.21	3.32
Pure gelat.	1.68....	1.68	1.68

Salt	Concentration			
	⅛ norm.	¼ norm.	½ norm.	1 norm.
Pure gelat.	1.88	1.70	1.83	1.71
NaCl	1.76	1.71	1.74	1.59
KCl	1.80	1.67	1.60	1.51
NH_4Cl	1.73	1.69	1.60	1.51
Pure gelat.	1.65	1.68	1.76	1.70
$NaNO_3$	1.63	1.57	1.56	....
KNO_3	1.65	1.53	1.52	1.48
NH_4NO_3	1.61	1.52	1.49	1.45

	Concentration			
	1/16 norm.	⅛ norm.	¼ norm.	½ norm.
LiCl	.....	1.73	1.78	1.66
$MgCl_2$	.....	1.76	2.00	1.88
Li_2SO_4	1.85	1.92	2.15	....
$MgSO_4$	1.90	2.12	2.42	....

B. DIFFERENCES BETWEEN INTERNAL FRICTION OF SALT-GELATINE AND PURE 1 PERCENT GELATINE

	Na	K	NH_4	Mg	Li
SO_4 1/16 norm.	—	—	—	+0.22	+0.17
SO_4 ⅛ norm.	+0.33	+0.09	+0.17	+0.44	+0.24
SO_4 ¼ norm.	+1.01	—	+0.48	+0.94	+0.47
SO_4 ½ norm.	+7.63	—	+1.64	—	—
Cl ⅛ norm.	....	....	−0.15	+0.10	+0.05
Cl ¼ norm.	−0.12	−0.08	−0.01	+0.20	−0.02
Cl ½ norm.	+0.01	−0.03	−0.23	+0.32	+0.20
Cl 1 norm.	−0.09	−0.20	−0.20	—	—
NO_3 ⅛ norm	−0.12	0.00	0.04	—	—
NO_3 ¼ norm.	−0 02	−0 15	−0 16	—	—
NO_3 ½ norm	−0.11	−0.24	−0.27	—	—
NO_3 1 norm.	−0.20	−0.32	−0.25	—	—

The plus sign means that the internal friction of the salt-gelatine is greater than that of the pure gelatine, and the minus sign the reverse.

which have stood for an hour. Table 23, B, details the difference in viscosity between salt-gelatine and pure gelatine. If the difference is positive it means that the viscosity of the gelatine has been increased by adding the salt, while if it is negative it means that the viscosity has been reduced to below that of pure gelatine.

It appears that sulphates in all concentrations increase the internal friction of gelatine, while chlorides and nitrates decrease it, with the exception of $MgCl_2$ and LiCl in higher concentrations. The exact concentration of the salt, however, plays an important part, especially in the chlorides which in medium concentrations (about 1/4 normal) show a maximum of viscosity which sometimes exceeds that of pure gelatine. Further details may be found in the tables and curves.[1]

If the anions of the added salts are arranged according to their effect we obtain the series:

$$SO_4 > Cl > NO_3$$

In the case of the cations variations occur with different concentrations. If we choose the values found for 1/8 normal solutions we find that the sulphates and the chlorides arrange themselves as follows:

$$Mg > Na > Li > NH_4 > K$$

Ample opportunity will be found later, to return to these "ionic series," which in honor of the investigator who discovered them are now known as the Hofmeister series. There we shall also find that the complicated influence of the concentration of a salt is not an accidental or an exceptional one, but an expression of general characteristics of the relation between any salt and a change in the state of the colloid system.

P. von Schroeder (*l.c.*) has investigated the important influence of acids and alkalies on the viscosity of gelatine solutions. His findings are detailed in Table 24 and Fig. 32. The influence of concentration is again complex, for at certain low concentrations (1/256 normal for HCl and 1/128 normal for NaOH) a maximum viscosity is attained, while at concentrations above 1/32 normal a viscosity below that of pure gelatine is observed.

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[1] It should again be emphasized that pure gelatine would, perhaps, show totally different results.

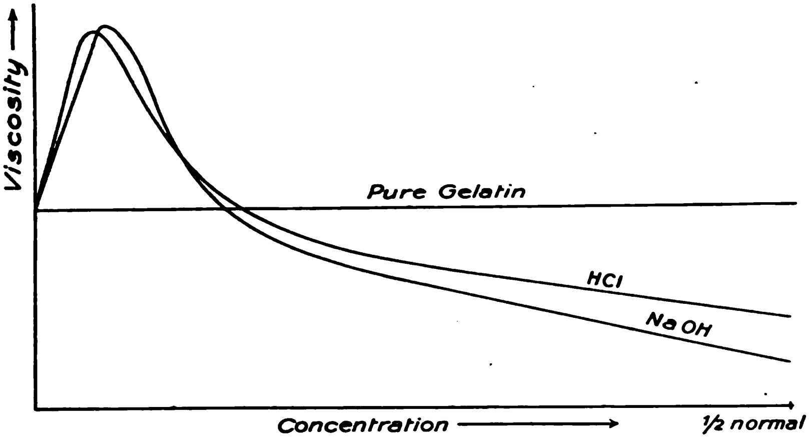

Fig. 32.—Effect of HCl and NaOH upon the viscosity of gelatine. (According to *P. von Schroeder.*)

Table 24.—Influence of HCl and of NaOH on Viscosity of Gelatine (According to P. von Schroeder)

HCl		NaOH	
Concentration	**Viscosity**	Concentration	Viscosity
0	1.40	0	1.40
1/512 norm.	1.55	1/512 norm.	1.52
1/256	1.76	1/256	1.60
1/128	1.68	1/128	1.79
1/64	1.58	1/64	1.62
1/32	1.42	1/32	1.38
1/16	1.25	1/16	1.25
1/8	1.17	1/8	1.10
1/4	1.12	1/4	1.10

Similar effects of concentration, more especially of the alkalies, on the viscosity of soap solutions have been observed by F. Bottazzi and C. Victorow (*l.c.*).

14. Effect of Added Substances on Internal Friction of Emulsoids; Behavior of Protein Solutions.—Through the work of E. Laqueur and O. Sackur (*l.c.*), W. B. Hardy (*l.c.*) and others, and especially through that of Wo. Pauli and his coworkers (*l.c.*), we have become better acquainted with the behavior of various protein solutions such as those of serum albumin, egg albumin, globulin and casein in the matter of their viscosity when subjected to the effects of added chemical substances. These solutions belong to the emulsoids. Time alone changes their internal friction, yet these changes take place so rapidly that the final viscosity value is reached within a few minutes. Because of this and because the proteins can be isolated and better purified than gelatine, for example, they adapt themselves especially well to a study of this important problem.

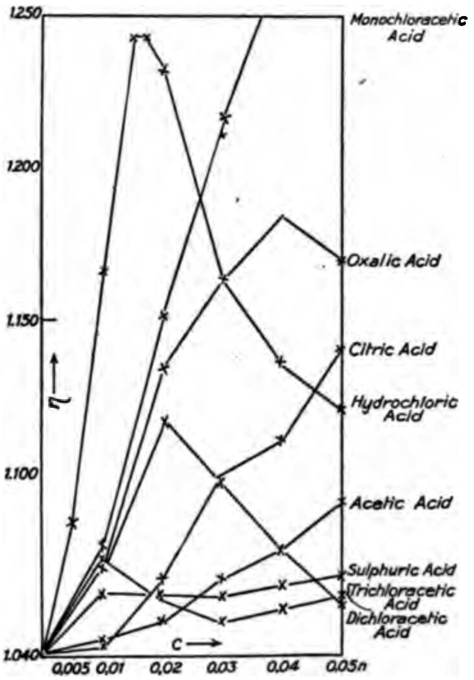

FIG. 33.—Influence of acids upon the viscosity of serum albumin. (According to *Wo. Pauli* and *H. Handovsky*.) η means viscosity.

The most striking fact that the study of the influence of electrolytes on the viscosity of purified proteins has brought out is *the enormous change in viscosity which is produced by traces of electrolytes*. This is especially true of acids[1] and alkalies which

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[1] Regarding the effect of acids, more especially of acetic acid on protein, see the paper of L. Zoja, Koll.-Zeitschr., 3, 249 (1908).

TABLE 25.—A. INFLUENCE OF ACIDS ON VISCOSITY OF SERUM ALBUMIN
(According to Wo. Pauli and H. Handovsky)[1]

Concentration	Internal friction					
	HCl	Citric acid	Oxalic acid	Sulphuric acid	Trichloracetic acid	Acetic acid
0.00 norm.	1.0409	1.0409	1.0409	1.0409	1.0409	1.0409
0.005	1.0832	....	....	....	1.0511	....
0.01	1.1660	1.0442	1.0688	1.0613	1.0725	1.0456
0.015	1.2432	....	....	....	....	....
0.017	1.2432	....	....	......	....	....
0.02	1.2323	1.0661	1.1337	1.0613	1.0594	1.0518
0.03	1.1647	1.1002	1.1634	1.0604	1.0525	1.0658
0.04	1.1356	1.1112	1.1852	1.0638	1.0564	1.0751
0.05	1.1206	1.1408	1.1700	1.0656	1.0603	1.0906

B. INFLUENCE OF BASES ON VISCOSITY OF SERUM ALBUMIN
(According to Wo. Pauli and H. Handovsky)

Base	Concentration	Friction increase in per cent.	Concentration, $OH'.10^{-5}$
Sodium hydroxide..........	0.01 norm.	78	960
	0.02	151	1900
	0.03	195	2805
Ammonia.................	0.01 norm.	19	49
	0.03	23	82
	0.05	28	108
Triethylamine.............	0.01	20	85
	0.03	28	148
	0.05	33	196
Ethylamine...............	0.01	37	214
	0.03	65	390
	0.05	83	465
Methylamine...	0.01	40	204
	0.05	76	442
Diethylamine.	0.01	52	308
	0.03	103	564
	0.05	146	800
Piperidine................	0.01	53	334
	0.03	109	627
	0.05	151	825
Tetraëthylammonium hydroxide................	0.01	116	922
	0.03	221	2718
	0.05	230	4490

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[1] See H. Handovsky, Koll.-Zeitschr., 7, 268 (1910).

show a behavior entirely analogous to that discussed in connection with gelatine on p. 173. Thus Wo. Pauli and H. Handovsky (*l.c.*) found that the addition of 0.015 normal HCl suffices to raise the viscosity of a serum albumin solution from 1.0623 to 1.2937, in other words, more than 20 percent. With alkalies, a concentration of 1/500 normal tetraëthylammonium hydroxide is enough to increase the viscosity by 230 per cent. Table 25 and Figs. 33 and 34 may serve to illustrate these facts.

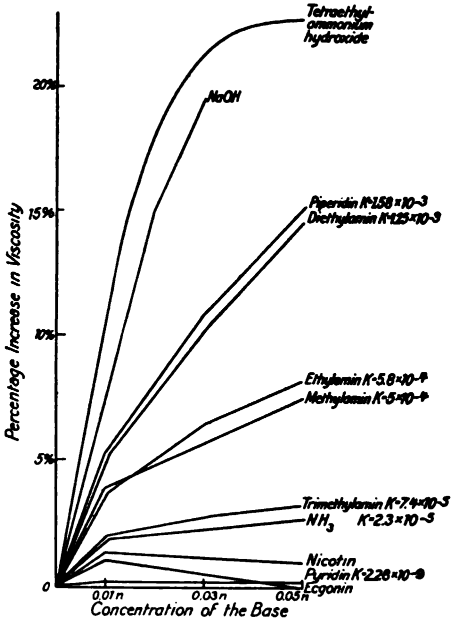

FIG. 34.—Influence of bases upon the viscosity of serum albumin. (According to (*Wo. Pauli and H. Handovsky.*)

So far as the effect of salts is concerned, it is found that this is different depending upon whether neutral, acid or alkaline albumin is used (Wo. Pauli). The relations are complicated especially when the effects of different concentrations of acids and alkalies as well as of salts are considered. It remains for future investigators to give us a clear and comprehensive presentation of this subject.

The following features deserve emphasis: Neutral salts always lower the viscosity of neutral protein (Wo. Pauli). This behavior is analogous to the effects of salts on the viscosity of suspensoids (see p. 152).

When we deal with acid albumin it is found that the anions of the neutral salts play a greater rôle than do the cations. Salts usually *lower* the viscosity, though complicated concentration relations appear. With a common cation the anions decrease the viscosity in the following order:

$$C_2H_3O_2 > SO_4 > SCN > NO_3 > Cl$$

[E. Laqueur and O. Sackur (*l.c.*), W. Frey (*l.c.*), H. Procter,[1] L. Zoja (*l.c.*), Wo. Pauli (*l.c.*) and others.]

The reverse is true with alkali albumin, where the cations play the chief part. From a qualitative point of view all the salts bring about a decrease in viscosity, but when the effects of equal amounts of salts are compared a greater decrease is noted in alkali albumin than in acid albumin. The salts of the alkali earth metals exert a stronger influence than those of the alkali metals.

15. Influence of Added Substances on Viscosity of Emulsoids. Effects of Non-electrolytes and Mixture of Dispersing Media.—*Non-electrolytes in low concentrations* usually change the viscosity of emulsiods only to the extent in which they increase the viscosity of the pure dispersion medium (S. J. Levites, Wo. Pauli, etc). Yet it is not impossible for non-electrolytes even in low concentrations to influence the viscosity somewhat. Thus Handovsky found that caffeine causes a very perceptible increase in the viscosity of acid albumin.[2] We need more experiments in this field.

In greater concentrations the addition of non-electrolytes causes very perceptible non-additive changes in viscosity. J. Simon (*l.c.*), for example, found alcohols, acetone, etc., to increase markedly the viscosity of albumin solutions. In future studies of these phenomena it might be well to subtract from the observed changes in viscosity those increases which result from mere mixing of the alcohol with water. Only then will the true changes in visocsity due to the change in the colloids themselves be clearly evidenced.

Several albumins, such as the zein of Indian corn, are remarkable in that they dissolve neither in water nor alcohol, but in a mixture of the two.[1] It would be interesting to study the viscosity behavior of such systems. The same is true of many dyes which although soluble in each of the pure solvents show different degrees of dispersion and even different types of colloidality in the two.[2]

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[1] H. Procter, Koll.-Zeitschr., 3, 307 (1908).

[2] Morphine, alcohol in low concentration, etc., probably produce similar effects.

16. Theory of Viscosity of Emulsoids.—The only attempt to deduce a rational formula for the viscosity of a system of two liquid phases has been made by E. Hatschek.[3] By considering a system in which the disperse phase is present in such amount that the structure is necessarily polyhedral, and making certain assumptions regarding the behavior of such a system when sheared, he arrives at the following expression:

$$\eta^1 = \eta \frac{\sqrt[3]{A}}{\sqrt[3]{A} - 1}$$

where η^1 is the viscosity of the system, η that of the continuous phase (dispersion medium) and A the ratio: total volume/volume of disperse phase.

The curve defined by this equation is hyperbolic in appearance, and η^1 increases rapidly as A approaches unity, in other words as the volume of disperse phase approaches the total volume.

The formula can be applied directly only to emulsions, in which A is known, but has hardly been tested in that respect. To apply it to emulsoids, it is necessary first to make assumptions regarding the *volume* of disperse phase, since in general only the weight of dispersed matter is given. The simplest assumption is obviously that the disperse phase "swells" by taking up a definite amount of dispersion medium (at constant temperature), in other words that the volume of disperse phase is a constant multiple of the weight of dispersed matter. This assumption has proved to give consistent results over a more or less extensive range of concentrations for sols of glycogen, casein,[4] and various serum proteins.[5]

On the other hand, the formula fails in the case of various colloids showing very high viscosities, such as rubber or nitrocellulose in organic solvents, where the assumption of a constant association factor proves quite unworkable. On theoretical grounds M. von Smoluchowski considers that the method used in deducing the formula cannot lead to a universally valid expression.

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[1] See the detailed paper of G. Galeotti and G. Giampalmo, Koll.-Zeitschr., **3**, 118 (1908), where references to the literature may also be found.

[2] H. Freundlich and W. Neumann, Koll.-Zeitschr., **3**, 80 (1908).

[3] E. Hatschek, Koll.-Zeitschr., **8**, 34, 1911.

[4] E. Hatschek, Trans. Faraday Soc., **57**, 56 (1913).

[5] H. Chick, Biochem. Journ., **7**, 261 (1914).

S. Arrhenius[1] has shown on a large number of examples that his well-known logarithmic formula:

$$\log \eta = \theta \, C$$

where θ is a constant and C the "molecular concentration," can be used for expressing the viscosity of emulsoid sols with remarkable accuracy. As the molecular weights of the dispersed phases are unknown, C can only be calculated by making simplifying assumptions, and the introduction of "molecular concentrations" appears unjustified in the case of systems which we have throughout considered to be sub-molecularly dispersed. The formula can therefore hardly be anything but an interpolation formula; but for colloids in aqueous dispersion it leads to remarkably constant values both for θ and for the hydration factors, which latter are of the same order of magnitude as for hydrated salts. The formula however also fails entirely for the above mentioned sols in organic solvents, the association factor becoming variable, and even negative in some cases.

A generally valid formula—either rational or empirical—for representing the viscosity of emulsoid sols is therefore still lacking, and it may be worth mentioning that M. von Smoluchowski (*l.c.*) does not consider the prospect of deducing the former very hopeful.

17. Viscosity and Electrical Charge of Disperse Phase.—E. Laqueur and O. Sackur (*l.c.*), W. B. Hardy (*l.c.*) and especially Wo. Pauli (*l.c.*) pointed out long ago that the electric charge of protein particles greatly affects the viscosity of their solutions. These investigators hold the electrically or electrochemically charged particles in these solutions to spring from an electrolytic dissociation similar to that observed in molecularly dispersed, slightly dissociated systems. As will become more evident in the chapter on the electrical properties of colloid systems, this assumption has proved both satisfactory and fruitful in explanation, for example, of the variations in viscosity caused by added substances. It may be said that when the viscosity of a neutral emulsoid rises on the addition of some substance, this is due chiefly to an increase in the number of dissociated (electrically charged) colloid particles. The correctness of this view is at once evidenced when we recall to mind the striking increase in the viscosity of gelatine, soap, or protein solutions when small amounts of acids or alkalies are added to them. The decrease in viscosity observed in higher concentrations of the acids and alkalies follows the decrease in dissociation. The effect of salts in lowering the viscosity of acid- and alkali-colloids corresponds with the effect of salts in depressing ionization when a common ion is introduced.[1] Table 25 (p. 175) may serve to show the general parallelism between concentration of OH ions and viscosity. Certain exceptions to the general rule are, however, to be noted, as in the case of piperidine.

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[1] S. Arrhenius, Meddelanden fran K. Vetenskapak. Nobelinstitut, 3, 1916.

The well-grounded fact that ions are more strongly hydrated than electrically neutral undissociated molecules explains why increase in dissociation and increase in viscosity go hand in hand. As a result of the magnetic field about the charged particles, or at least through its increase, we may imagine the solvent to be held more closely in the solvent envelopes about the separate particles. Thus also will the internal friction be increased and the separate particles become less mobile for now the charged particles have larger envelopes of the dispersion medium about them. But let us not fail to point out that it does not seem safe to say that this direct application of electrochemical laws will, in the future, show itself to be entirely adequate. Nevertheless the ability of these laws to elucidate at least some of the complicated relations observed shows them to be at least partly active.

Future investigators may reveal great discrepancies between the laws governing the behavior of colloid systems and the electrochemical laws which apply to molecular and supermolecular disperse systems. Notwithstanding isolated analogies, colloid systems may be found to be governed by electrochemical laws which are not subordinate to those governing molecular systems but coördinated with them. Great variations from normal electrochemical behavior are already known in the case of suspensoids.[1] We can discuss these questions to greater advantage when we come to consider the electrical properties of colloid systems.

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[1] For a discussion of the electrochemical side of these views see the textbooks of physical chemistry.

18. Viscosity and Degree of Dispersion; Viscosity of Coarse and Complex Dispersions.—Only few observations are available on the theoretically important relation between degree of dispersion and viscosity, and no systematic study has as yet been made of any number of systems with progressively varying degrees of dispersion. A priori one would expect the viscosity of a dispersoid to grow with every increase in the amount of contact surface, in other words, with the degree of dispersion. It is here assumed that the particles of the disperse phase move about with greater difficulty than do the particles of the dispersion medium itself. The dispersion medium, held in the often-mentioned surface membranes, must have in addition to its usual characteristics a decreased mobility. Experimental evidence can be cited to support this view. The experiments described on p. 152, dealing with the decrease in the viscosity on ageing or the addition of salts, show a distinct parallelism between decrease in degree of dispersion and decrease in viscosity. K. Beck and K. Ebbinghaus[2] found that coarse emulsions of castor oil in water did not greatly change the viscosity of the water, but after gum arabic or similar substances had been added which permitted the attainment of higher dispersion, the viscosity rose considerably above that of the oil or the pure gum solution. The increase amounted to 44 percent. The fact that cellulose becomes slimy and viscous with long grinding indicates the same thing. G. Buglia[3] found milk to show a distinct increase in viscosity after being "homogenized," that is to say, after having its fat finely divided by being squirted against an agate plate. A. Martici[4] has studied the viscosity of oil emulsions in soap water and found that their viscosity increases as the oil droplets become smaller.

But observations can also be cited to support the opposite view. Cases are known in which the viscosity increases as the demonstrate the influence of concentration on the viscosity of coarse emulsions, for this varies within the concentration limits of 0 to 0.75 percent water from that of a liquid soap to that of a "solid" lubricant. Another illustration of the latter has been found by K. Beck (*l.c.*) and his co-workers in their work on emulsions of acacia water and castor oil. While small amounts of emulsified castor oil but slightly increased the viscosity of the gum arabic solutions certain higher concentrations caused sharp increases. Fig. 35 illustrates this behavior which is fully analogous to that observed in emulsoids. Excellent analogies for the great effect of temperature on the viscosity of lyophilic colloids can also be found in the case of the coarser emulsions. J. Friedländer (*l.c.*) and V. Rothmund (*l.c.*) found the viscosity of critical fluid mixtures to be very sensitive to temperature. The temperature coefficient of viscosity in these ranges is three to five times as great as in those in which the system has lost its emulsion nature. The machine oils already mentioned may serve as further illustrative material. Their decrease in viscosity with increase in temperature is so great that one may distinguish a softening point and a dropping point, the two at times lying but one degree apart.

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[1] See Wo. Ostwald, Koll.-Zeitschr., **7**, 132 (1910).

[2] K. Beck, Zeitschr. Physik. Chem., **58**, 409 (1907); K. Ebbinghaus, Diss., Leipzig, 1907.

[3] G. Buglia, Koll.-Zeitschr., **2**, 353 (1908).

[4] A. Martici, Arch. di. Fisiol., **4**, 133 (1907).

This indicates that their viscosity may fall from that of a solid to that of a liquid within the scope of a few degrees, a suddenness of change which is similar to that observed in the melting points of solids. Finally, attention should be called to a third system, namely, that of an alcoholic solution of rosin containing a little water, investigated by J. Friedländer. This also possesses a relatively large temperature coefficient, namely, one of 5 to 6 percent per degree of temperature against that of about 2 percent for water.

19. Viscosity and Type of Disperse Phase.—We have thus far considered the viscosity relations of only the more common and important dispersoids, namely, those having the composition liquid + solid and liquid + liquid. It should, however, be remembered that remarkable increases in viscosity of a liquid dispersion medium may be caused by finely dividing a gaseous phase in it as illustrated by the mechanical properties of foams which often have many of the characteristics of a solid. We have of course to take into account that strictly two-phase systems of the type liquid + gas are hardly known and that the stability of most foams is closely associated with their so-called adsorption phenomena by virtue of which the gas bubbles condense dissolved substances upon their surfaces with consequent formation of solid films. Yet such adsorption processes are, in many cases, completely reversible and the fluid nature of the membranes is preserved throughout. Thus saponin foam melts down to a homogeneous fluid perfectly free from coagula, and egg-white may be freed of the threads and coagula present in it in its natural state by beating it to a foam. The greater part of the foam subsequently melts down to a solution perfectly free from flocculi. This is evidence for the fluid nature of the walls of the foam. The preparation and detailed investigation of colloid foams would evidently be of great interest to general colloid chemistry.[1]

If one compares the internal friction of the three typical dispersoids having a fluid dispersion medium, it is found that a low initial viscosity of disperse phase by no means precludes the attainment of high viscosity values for the whole system. In fact, if colloid dispersoids are compared with each other, it is found that emulsoids usually exhibit a higher viscosity than the suspensoids having the same concentration and, in view of the great stability of highly dispersed foams, it even seems as though such when in a colloid degree of dispersion might show still higher viscosity values. We must of course distinguish between high viscosity and the value of other physical properties such as hardness. Paradoxical as it may seem, it even appears as though viscosity of the dispersion medium and viscosity of the disperse phase may be only of indirect significance, for it seems probable that the properties of the different surfaces (liquid-solid, liquid-liquid, and liquid-gaseous) and not the low viscosity value of the disperse phase itself are primarily responsible for the viscosity of the dispersoid as a whole.

§26. Surface Tension of Colloid Solutions

1. **General Remarks.**—A closed two-phase dispersoid has a series of surfaces. The most important is the one between the

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[1] For some observations on fine foams see Wo. Ostwald, Koll.-Zeitschr., **1**, 333 (1907). Systems belonging to this class are also described by Schroeder, Poggendorf's Ann., **137**, 76 (1869); see also the patent of J. Weinmayr, described in Chem. Centralbl., 586 (1910).

disperse phase and the dispersion medium. There is, in addition, the surface between the whole dispersoid and its surroundings, in considering which we must distinguish between the surface bounding the dispersoid and its vapor and that between the dispersoid and the walls of the vessel, etc. At the present time, however, the sense and value of only a few of these tensions are known; in fact quantitative measurements are available of but a single surface tension, namely, that of the positive tension in the surface between the dispersoid and its vapor.

2. Experimental Facts.—Investigations show that the positive surface tension[1] of a colloid solution at its free surfaces may be more, or less, or equal to that of the pure dispersion medium (Rayleigh,[2] A. Pockels,[3] W. Ramsden,[4] G. Quincke,[5] H. Picton and S. E. Linder,[6] L. Zlobicki,[7] W. Frei,[8] G. Buglia,[9] F. Bottazzi and C. Victorow[10]). Usually the tension is less.

The surface tension of water is increased by gum arabic, starch and plum gum. It is lowered by gelatine, glue, egg-albumin, dextrin, cherry and sweet cherry gum. It is greatly lowered by fats, fatty acids, soaps, resins, tannic acid, etc. Tables 26 and 27 taken from G. Quincke and L. Zlobicki may serve in illustration.

Both the increase or the decrease in surface tension follows the concentration of the colloid. Traces of fatty acids, of soaps, etc., suffice to lower greatly the surface tension of water as seen in Table 26. The surface tension of colloid solutions as of liquids in general decreases as the temperature rises but, as Table 27 shows, the decrease is much more marked than in the case of the pure dispersion medium alone.

The type of the disperse phase is of particular importance in determining the change in the surface tension of the pure disper-

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[1] The textbooks of physics and physical chemistry should be consulted for methods of measuring the positive surface tension.

[2] Rayleigh, Proc. Roy. Soc., **47**, 364 (1890).

[3] A. Pockels, Nature, **46**, 418 (1892); Drude's Ann. d. Physik., **8**, (1902).

[4] W. Ramsden, Engelmann's Arch. f. Anat. und Physiol. Abt. f. Physiol., 517 (1894); Z. f. physik. Chem., **47**, 341 (1902); Proc. Roy. Soc., **72**, 156 (1904).

[5] G. Quincke, Wiedemann's Ann., **35**, 582 (1888) Ber. d. Berl. Akad. d. Wissensch., **38**, 493, 858 (1901); Drude's Ann. d. Physik., **7**, 631 (1901); *ibid.*, **9**, 969 (1902); *ibid.*, **10**,507 (1903); *ibid.*, **11** (1904).

[6] H. Picton and S. E. Linder, Journ. Chem. Soc., **87**, 1924 (1905).

[7] L. Zlobicki, Bull. Acad. Sc. Cracovie, Juli, 488 (1906).

[8] W. Frei, Zur Theorie der Hämolyse, Diss., Zurich, 1907; Transvaal Medic. Journ., August, 1908.

[9] G. Buglia, Biochem. Zeitschr., **11**, 311 (1908).

[10] F. Bottazzi and C. Victorow, Rend. R. Ac. Linc., **19**, 659 (1910).

Table 26.—Surface Tensions of Colloid Solutions at About 20°
(According to G. Quincke)

Substance	Specific gravity	Surface tension against "air"
Water	1.0000	8.253
Egg-albumin	1.0365	5.934
	1.0384	5.370 to
	1.0384	4.913
Aqueous bile solution (9 percent)	1.10133	5.070
Venetian Soap		
1/4000 percent	0.9983	2.681
1/400 percent	0.9992	2.672
1/40 percent	1.0009	2.563
Tannic acid, 10 per cent	1.0352	5.857
Gum arabic, 20 per cent	1.0708	7.603
Isinglass very dilute	1.0000	6.790
Gelatine very dilute	1.0000	7.272
Agar very dilute	1.0000	7.842

Table 27.—Surface Tensions of Colloid Solutions
(According to L. Zlobicki)

2 Grams gelatine in 100 cc. solution			2 Grams gum arabic in 100 cc. solution		
Temp.	Surface tension in mg./mm.		Temp.	Surface tension in mg./mm.	
	Solution	Water		Solution	Water
0.0	6.62	7.69	0.0	8.66	7.69
11.3	6.21	7.52	6.6	8.47	7.59
17.0	5.98	7.43	17.0	8.16	7.42
24.5	5.70	7.32	24.0	7.75	7.33

sion medium. This is indicated by the fact that all the above-mentioned examples are emulsoids. Coarse suspensions and suspensoids, hardly alter the surface tension of the dispersion medium. H. Picton and S. E. Linder (*l.c.*) found suspensoid arsenious trisulphide, even in concentrations of 2 percent, and dilute iron hydroxide to produce so slight a decrease in the surface tension of pure water that it scarcely exceeds the experimental error. N. Sahlbom[1] obtained analogous results. L. Zlobicki (*l.c.*) found coarse aqueous suspensions of emery, mastic and gamboge and colloid suspensions of silver and platinum to have the same surface tension as the pure dispersion medium. The temperature coefficient of the surface tension of these systems was also the same as that of the pure dispersion medium.

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[1] N. Sahlbom, Kolloidchem. Beih., 2, No. 3 (1910).

These results seem to show that only emulsoids decrease the surface tension of their dispersion media. This difference can, in fact, be used as a means for distinguishing the two classes of colloids from each other. Here again is evidenced the close connection between emulsoids and molecular-dispersoids in that the latter also always exhibit a surface tension different from that of their pure solvents.

As already indicated (p. 55), the same chemical substance may assume either emulsoid or suspensoid properties in different dispersion media. Thus soaps, many dyes, etc., form emulsoids in water while they form suspensoids in alcohol. One would expect this distinction to show itself in the surface tension behavior of the different solutions when compared with that of their pure dispersion media, which, in fact, it does, as H. Freundlich and W. Neumann[1] have found. Table 28 illustrates this interesting fact in that it shows that the surface tensions of the aqueous dispersion media are noticeably decreased while those of the alcoholic solutions show no change, or if anything, a slight increase.

TABLE 28.—SURFACE TENSIONS OF COLLOID DYES IN WATER AND IN ALCOHOL (According to H. Freundlich and W. Neumann)*

Water		Alcohol	
Substance	Surface tension	Substance	Surface tension
Water	75.0	Alcohol	21.9
Night-blue	68.3	Night-blue	22.3
“	67.4	“	22.2
Congo red	74.8	Crystal violet	22.2
Crystal violet	72.7	“	22.2
New fuchsin	75.3	New fuchsin	22.2
Diamond fuchsin	74.6	“	22.1
Rhodamin**	74.4	Rhodamin	21.9
		“	22.9

* The surface tensions were measured by the rise in capillary tubes.
** This dye is probably molecularly dispersed.

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[1] H. Freundlich and W. Neumann, Koll.-Zeitschr., 3, 80 (1908).

The surface tension of emulsoids is changed by the addition of dispersed substances. This was to be expected from their effect on viscosity. The addition of small quantities of hydroxyl ions raises, while the addition of hydrogen ions decreases the surface tension of neutral gelatine or neutral blood serum (G. Buglia, W. Frei). F. Bottazzi and C. Victorow observed NaOH to affect greatly the surface tension of soap solutions, a behavior which is the image of the corresponding one regarding viscosity. Very low concentrations caused a great decrease in tension; higher concentrations led to an increase which soon reached a maximum to give way to a second more gradual decrease. W. Frei found the anions SO_4, Cl, NO_3 and the cations Na, K, Mg and Ca to increase the surface tension of neutral gelatine solutions in almost the same order in which they increase that of pure water. It is an interesting fact that the order of the anions is reversed depending upon whether the gelatine is acid or alkaline.

Several interesting investigations show how varied and complicated are the relations when we also consider the changes in the other surface tensions of the dispersoid, especially if it is of the type fluid + fluid in which we are able to measure experimentally the interfacial tension between the disperse phase and dispersion medium. According to G. N. Antonow[1] and W. C. McC. Lewis[2] we know of two cases, namely, water-ether and aqueous glycocolate solution-mineral oil, in which the tension at the interfaces *increases* with rising temperature instead of decreasing as is usually the case. Even though this was observed in the case of but slightly dispersed systems, there is no reason for not believing that temperature exerts a like influence in highly dispersed systems of the same composition. The decrease in capillary rise, with increasing temperature, observed by R. Schenck,[3] in cholesteryl-benzoate (a so-called crystalline liquid) may come under this head.

We have now to call attention to a factor which must be considered in measuring the surface tension of molecularly dispersed systems but which assumes a still greater importance in colloid systems. Willard Gibbs has formulated a theorem which has been confirmed at least qualitatively by other investigators. It states that *substances which lower the surface tension of the*

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[1] G. N. Antonow, Journ. Chim. physique, **5**, 372 (1907).
[2] W. C. McC. Lewis, Philos. Mag., **15**, 506 (1908).
[3] R. Schenck, Kristallinische Flüssigkeiten, 1129, Leipzig, 1901.

pure dispersion medium, tend to collect in its surface. Because of this rise in concentration the surface tension must, with time, become progressively lower wherefore it is conceivable that it may, under certain circumstances, attain a value different from the original present in the surface immediately after its formation. The latter surface tension, which can be measured only on freshly formed or constantly renewed surfaces is called the ***dynamic*** *surface tension;* that which is present after some time, the ***static.*** The distinction between these two surface tensions is of especial importance in colloid solutions because such very small amounts of many colloid substances are able to reduce so greatly the surface tension of the pure dispersion medium.[1]

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[1] See the recent work of Wm. C. McC. Lewis, Z. f. physik. Chem., **74**, 619 (1910) in which are detailed the surface tensions of colloid solutions against their own vapors and against the surface of various liquids.

CHAPTER VI

MECHANICAL PROPERTIES OF COLLOID SYSTEMS

III. MOVEMENT IN COLLOID SYSTEMS AND ITS RESULTS

§27. Brownian Movement

1. General Remarks.—The Fundamental Phenomenon.—Literature.—All dispersoids of a sufficiently great degree of dispersion and having a fluid or gaseous dispersion medium, show under the microscope and ultramicroscope a characteristic movement. This was discovered by the English botanist, R. Brown,[1] and has been named for him. Brownian movement is also known as "spontaneous" or "molecular" movement though the latter term should be used cautiously. The separate particles of the disperse phase exhibit a trembling and rotary movement and when the particles are very small, as in colloid solutions, the movement has been described by Zsigmondy as "dancing, hopping and skipping" in nature and also as "translatory" and "progressive." The movement of the smaller particles differs from that of the larger (microscopic) ones in that the former travel along straight lines and suddenly change their direction while the latter follow a more curved path.

The movements do not occur in one plane only but in all directions. As one observes the "optical cross section" of a preparation either microscopically or ultramicroscopically, the individual particles disappear and reappear as they move downwards and upwards.

Many pictures of this characteristic movement have been published. In Figs. 36, 37, 38, 39, and 40 are reproduced some particularly characteristic types of the movement according to V. Henri,[2] R. Zsigmondy[3] and O. Lehmann.[4] In picturing such movement in one plane we can, of course, show only the projections of the paths of the particles. To a discussion of more exact methods of determining and measuring these movements we shall shall return later (p. 197).

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[1] R. Brown, Philos. Mag. (1), **4**, 101 (1828); **6**, 161 (1829); **8**, 41 (1830); and also Poggendorf's Ann. d. Physik., **14**, 29 (1828).

[2] V. Henri, Compt. rend., **147**, 62 (1908). A review of the subject of Brownian movement, particularly as illustrated in the movements of the spherules of liquid rubber, may be found in his Le Caoutchouc et la Guta-percha, 2405, 1906 and 1908.

[3] R. Zsigmondy, Z. Erkenntnis d. Kolloide, 106, Jena, 1905.

[4] O. Lehmann, Molekularphysik., **1**, 264, Leipzig, 1888.

Examples of dispersions exhibiting Brownian movement are suspensions of gutta-percha, mastic, etc., prepared by adding water to very dilute alcoholic solutions;[1] suspensions of ultramarine, cinnabar, carmine, etc., in which the disperse phase is amorphous or crypto-crystalline; the contents of the chalk sacs to be found on either side of the spine in the frog, in which the disperse phase consists of definite prismatic crystals; metal hydrosols; metal sulphide hydrosols and other suspensoids. Milk and latex [O. Lehmann, V. Henri, (*l.c.*)] are examples of systems having a liquid disperse phase and showing Brownian movement. Brownian movement may also be observed in gas-solid dispersoids such as tobacco smoke, cooling ammonium chloride vapors and condensing metal vapors. It may also be observed in gas-liquid dispersoids as in fog.

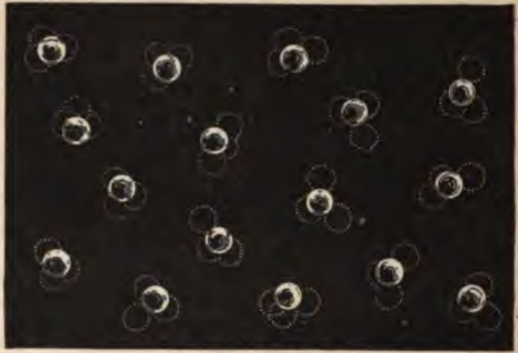

FIG. 36.—Brownian movement in milk. (According to *O. Lehmann.*)

Strong magnification is usually necessary to observe Brownian movement. Dark ground illumination together with ultramicroscopic methods are especially suited for the examination of colloids.

H. Molisch[2] has shown how, under favorable conditions, this movement may be detected with the naked eye. The latex of

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[1] See J. Perrin, Die Brownsche Bewegung und die wahre Existenz der Moleküle (Dresden, 1910) for methods of preparing suitable suspensions for the observation of the movement.

[2] H. Molisch, Koll.-Zeitschr., **2**, Suppl. I, 9 (1907); Zeitschr. f. wissensch. Mikros., **23**, 97 (1907); Sitz. Ak. Wiss. Wien, **116**, Abt. 1, März., 1907.

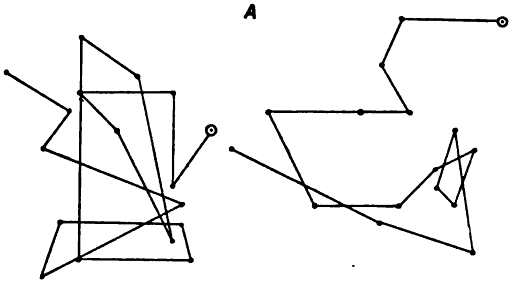

FIG. 37.—In a neutral medium.

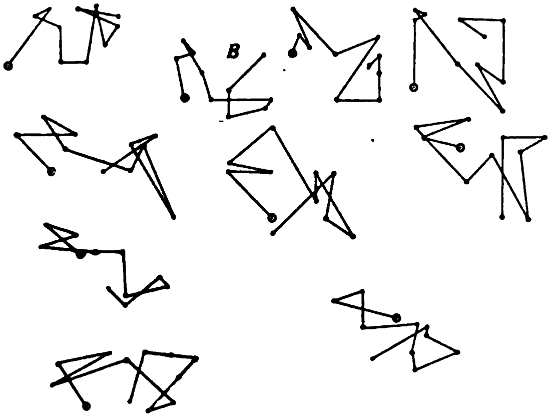

FIG. 38.—In an alkaline medium.

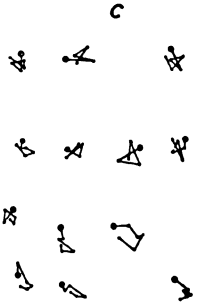

FIG. 39.—In an acid medium.

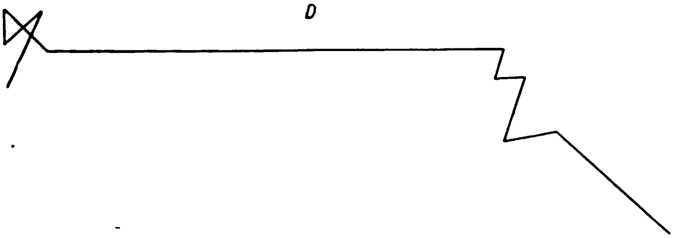

FIG. 40

FIGS. 37 TO 40.—Brownian movement. *A*, *B* and *C* are drawn from kinematographic photographs of gutta-percha particles. *D* represents the translatory Brownian movement of a gold particle having a diameter of about 10μμ. (According to ***R. Zsigmondy***.) Figures *A*, *B* and *C* are enlargements of 34,000 to 1; figure *D* one of 5000 to 1.

the spurge (Euphorbia) is especially adapted for this. A drop of the material is placed upon a slide and held at a good visual distance in a vertical or almost vertical position while sunlight or the concentrated light from an arc is allowed to fall upon it at a slight angle. When properly placed "the molecular movement (Brownian movement) of the resin particles appears in the form of a peculiar trembling, a lively dance, and a swarming of the microscopic particles giving rise to a beautiful play of colors. Finely ground india ink in water may also be recommended for this experiment" (H. Molisch, *l.c.*).

Directions for observing Brownian movement with the aid of a projection-apparatus have been suggested by J. Perrin (*l.c.*).

Since its discovery in 1827, Brownian movement has been much investigated both experimentally and theoretically. The rather comprehensive literature, for it comprises more than 100 articles, cannot be quoted here. We shall refer to some specific papers only; for reviews of the subject the reader must look elsewhere.[1]

2. The Independence of Brownian Movement of External Sources of Energy.—When trying to account for the forces responsible for these remarkable movements one is at first inclined to think them due to the effect of external agencies such as vibrations, differences in temperature, etc., due to unequal irradiation, evaporation, surface tension movements, chemical changes, etc. Chr. Wiener[2] and G. Guoy[3] are to be especially mentioned of those who have made critical investigations to show that none of these factors is responsible for Brownian movement. We cannot go into a detailed restatement of the many experiments that prove *the fundamental independence of Brownian movement of external sources of energy*. Only the following points are mentioned as of particular importance. In connection with them it must be kept in mind that all the various factors mentioned of course *influence*

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[1] See, for example, O. Lehmann, Molekularphysik., **1**, 264, Leipzig, 1888, where a detailed review of the older papers up to 1888 may be found; The Svedberg, Nov. Act. Soc. Sc. Upsaliensis, Ser, IV, **2**, 125 (1907) where 50 articles are referred to; Koll.-Zeitschr., **7**, 1 (1910), where references to newer work and methods of observation are found; J. Perrin, Kolloidch. Beih., **1**, Heft 6–7 (1910) also available in monograph form and dealing particularly with French workers; W. Mecklenburg Die experimentelle Grundlegung der Atomistik, Jena, 1910, etc.

[2] Chr. Wiener, Poggendorf's Ann., **118**, 79 (1863).

[3] G. Gouy, Journ. de Physique, 2 Ser., **7**, 561 (1888); Compt. rend., **109**, 102 (1889); Revue génerale des Sciences, **1**, 1895.

the extent of Brownian movement but neither *positive nor negative* variations in them are capable of suppressing entirely the movement inherent in the particles themselves.

The effects of vibration, changes in temperature, evaporation, etc., in modifying Brownian movement, may be excluded by working in basements, mines and fields (G. Gouy, Chr. Wiener), with water baths and with sealed containers, etc.

The independence of Brownian movement of light effects may be proved by working with different kinds of light from which the heat waves have been carefully excluded [G. Gouy, R. Zsigmondy (*l.c.*, 1905)].

That mutual attractions and repulsions of oscillating particles, dependent, for example, upon differences in electrostatic charge, are not the cause of Brownian movement has been shown by Chr. Wiener (*l.c.*) and C. Fuchs.[1]

The Svedberg (*l.c.*) has shown on silver hydrosols that neither neutralization of the charge nor its reversal, as may be brought about through the addition of traces of electrolytes, have any effect upon the velocity of the particles. The amount and sign of the electric charge of such particles may be determined from their migration in an electric field. The following table illustrates the independence of Brownian movement of the sign and amount of the electric charge as determined by measuring the value of $2A$, of the significance of which more will be said later (see page 198).

TABLE 29.—INDEPENDENCE OF BROWNIAN MOVEMENT OF THE SIGN AND AMOUNT OF THE ELECTRIC CHARGE OF COLLOID SILVER PARTICLES

(According to The Svedberg)

Sign and amount of electric charge determined and measured from the speed of migration of the particles, μ/seconds: volt/cm.	Intensity of Brownian movement (value of $2A$)
+2.10	2.5
+0.26	2.5
−0.42	2.4
−1.76	2.4

J. Perrin (*l.c.*, 1910, 273) has also found that the addition of traces of acids to gutta-percha suspensions, which first neutralize and then reverse the sign of their original charge, has "no appreciable" influence on their Brownian movement.

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[1] C. Fuchs, Rep. d. Physik., **25**, 735 (1889).

The movement is not caused or markedly influenced by any chemical reactions occurring between disperse phase and dispersion medium. This is proved not only by the fact that all chemically heterogeneous substances thus far investigated exhibit the movement when sufficiently dispersed, but by the further fact that the intensity of the Brownian movement in a given dispersoid is always the same, in other words, does not change with ageing. If chemical reactions were responsible for the movements, say indirectly through changes in capillarity (as in the case of mercury droplets in contact with sulphuric acid and potassium bichromate) then the movements would cease after a time. As a matter of fact, solid particles and gas bubbles, suspended in liquid occluded in many minerals, and therefore of course, very old, show Brownian movement. (See for example G. Gouy, *l.c.*). Like considerations exclude all the capillary theories[1] of Brownian movement which at first glance are so plausible. At present, it is inconceivable why in a closed system an equilibrium should not ultimately become established between the participating surface tensions for example.

Finally, it should be mentioned that the *type* of the *disperse phase* or of the *dispersion medium* is not of decisive importance in bringing about Brownian movement provided the system is from the outset of a kind to permit it, in other words, is either liquid or gaseous. Not only solid and liquid particles but gaseous ones as well show Brownian movement in fluids. But solid and liquid particles show Brownian movement in gases also, as in smoke, in condensing metallic vapors, in fog, etc.[2] (L. J. Bodaszewski,[3] H. Molisch, (*l.c.*), F. Ehrenhaft,[4] M. de Broglie[5]). That Brownian movement is independent of the type of the disperse phase also proves that *density* is not of fundamental importance in its causation as already emphasized by the earlier writers, Chr. Wiener, G. Gouy, etc.

These investigations, often of a most painstaking nature, show that the source of energy for Brownian movement lies within the disperse system itself and is obviously of a very general nature for it evidences its effects under the most varied external conditions. Brownian movement is, however, observed only in disperse systems, more particularly only in such as have a high degree of dispersion. The kinetic hypothesis according to which gases and liquids are regarded as conglomerates of rapidly moving molecularly dispersed particles, has recently been applied to Brownian movement. In fact, some have seen in this direct evidence for the correctness of the kinetic theory as applied, say, to the movement of liquid particles. We return to this question on page 210. While really marvelling at the successful applications that have been made of this kinetic hypothesis, it seems to me not impossible that future investigations may yield another more universal and less hypothetical explanation of this spontaneous movement.

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[1] Such capillary theories of Brownian movement have been suggested by G. van der Mensbrugghe, Poggendorf's Ann., **138,** 323 (1869); C. Maltezos, Ann. chim. phys. (7), **1,** 559 (1894); Compt. rend., **121,** 303 (1895); G. Quincke, Verh. d. Naturforscher usw., 26, Düsseldorf, 1898; Beibl. Ann. d. Physik., **23,** 934 (1899) etc., and others.

[2] O. Lehmann, Molekularphysik., **2,** 5, Leipzig, 1888.

[3] L. J. Bodaszewski, Dingler's Polytechn. Journ., **239,** 325 (1881).

[4] F. Ehrenhaft, Sitz. Ak. Wiss. Wien., **116,** 1139, (1907), ibid März., 1909; Physik. Zeitschr., **12,** 308 (1909), etc.

[5] M. de Broglie, **148,** 1165, 1315 (1906); Le Radium 203, (1909).

3. More Exact Determination and Measurement of Brownian Movement.—Various methods have been devised for the exact quantitative study of this very irregular movement.[1] Evidently graphic representations in one plane can only show a part of the movement, viz., one projection of it. It may be assumed, however, that the movement in all directions is of the same nature. The paths of the Brownian movement of isolated particles have been traced by F. M. Exner (*l.c.*). He equipped his microscope with a drawing apparatus and followed the movements of the particles on a smoked glass with a needle. If the time required for a particle to traverse a certain path is noted with a stop watch and the path is then measured one obtains, by division, the average velocity of the particle.

Another ingenious method, devised by The Svedberg,[2] is based on the following principle. When a fluid dispersoid is allowed to flow at constant velocity and with sufficient speed through the field of a microscope or ultramicroscope one observes a whole series of light curves.[3] These are the optical after-images of the individual dispersed particles which themselves move too rapidly to be seen. The curves have a wave-like or zigzag form as shown in Fig. 41. Their deviation from the horizontal evidently is a measure of the intensity of oscillation occasioned by the spontaneous motion of the particles. The height of the crests or the amplitude ($= A$) may be measured directly with a micrometer, or be estimated. When the rate of flow is known, the average absolute velocity of a particle may be calculated[1] after the constant of the apparatus itself has been determined.[2] With the fluid at rest, $2A$ corresponds to the total deviation of the particle from its initial position.

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[1] See especially the critical presentation of The Svedberg, Koll.-Zeitschr., **7,** 1 (1910); J. Perrin, *l.c.*; St. Jahn, Jahrb. f. Radioakt., **16,** 235 (1909).

[2] The Svedberg, *l.c.*, also Z. f. Elektroch., **12,** 853, 909 (1906).

[3] Dark ground illumination, must, of course, be used.

Still more exact measurements may be obtained by photographic and especially by kinematographic means. With these, which M. Seddig,[3] V. Henri (*l.c.*), H. Siedentopf[4] and The Svedberg (*l.c.*, 1910) have used in different ways, the change in position of the particles with time, in other words, their oscillations, may be accurately measured. Seddig, Henri, Chaudesaigues, etc., determined the change of position of a particle by photographing a preparation at short intervals. Seddig photographed it twice every $\frac{1}{10}$ second, Henri, with kinematographic apparatus, on a moving film several times every $\frac{1}{20}$ second. The interesting apparatus of the last-named investigator is shown in Fig. 42. To the left is the kinematographic camera, in the middle, the ultramicroscope, to the right, the source of light, as an arc lamp. As the time is known, the average velocity of the particles may be

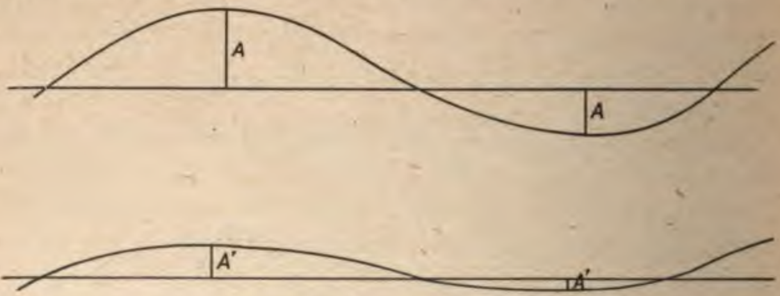

FIG. 41.—Diagram illustrating the measurement of Brownian movement.

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[1] For details regarding these measurements see especially The Svedberg, Nov. Ac. Soc. Sc. Upsaliensis, *l.c.*, 143.

[2] By an analogous method, M. de Broglie has measured the Brownian movement in gas suspensions.

[3] M. Seddig, Sitz. Marburger Ges., Nov., 1907; Physik. Zeitschr., **9**, 465 (1908); Habilitationsschrift, Frankfurt a. M., 1909.

[4] H. Siedentopf, Zeitschr. f. wiss. Mikrosk., **26**, 407 (1909).

determined very closely by measuring the plates and the changes in the position of the particles. Most of the paths of Brownian movement reproduced in Figs. 37 to 40 were obtained in this manner.

H. Siedentopf uses a falling photographic plate. In this wise he obtains curves as shown in Fig. 43, which correspond to those first observed by Svedberg. Svedberg (*l.c.*) has more recently used a photographic method in which the position changes are registered as points on a rotating film. For details his original paper must be consulted. Finally it should be mentioned that P. Chaudesaigues[1] and later J. Perrin in the extended work already referred to, also calculated the velocity by following the position changes of the particles at definite intervals with the aid of a drawing apparatus.

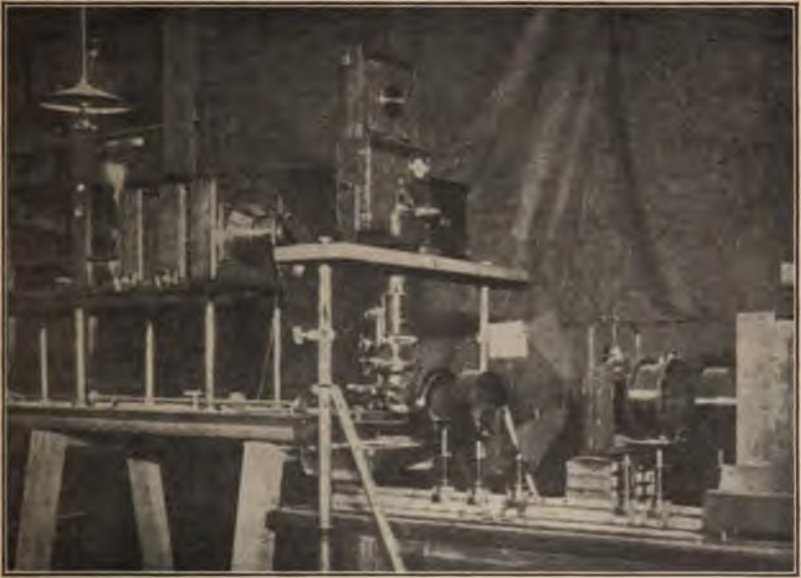

FIG. 42.—*V. Henri's* apparatus for photographing Brownian movement cinematographically.

The *rotary* motion which many particles show has been studied by J. Perrin.[2] To this end he measured the rotary movement of small excrescences, such as air bubbles, eccentrically attached to the larger globules of a mastic hydrosol in unit time.

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[1] P. Chaudesaigues, Compt. rend., **149**, 1044 (1908).

[2] J. Perrin, Compt. rend., **149**, 549 (1909).

By these methods that most characteristic property of Brownian movement, namely its velocity, can be accurately measured and the influence of different external conditions on it be studied.

4. Uniformity of Brownian Movement.—A law of fundamental importance to the theory of Brownian movement has been stated by Svedberg.[1] *The amplitude of movement is directly proportional to the period of vibration*, in other words, to the time required by a particle to complete a whole backward and forward vibration.

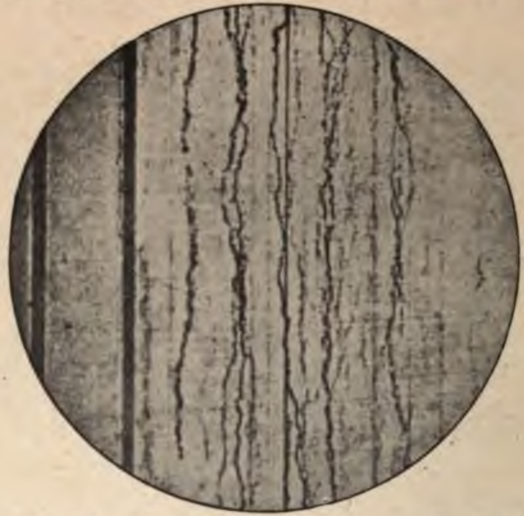

FIG. 43.—Brownian molecular movement. (According to *H. Siedentopf.*) Instantaneous exposure of a falling plate. Zeiss dark ground condenser.

If this is represented by $2A$, while by $2t$ is represented the period of vibration, the relation between the two may be expressed thus:

$$\frac{A}{t} = \text{const.}$$

This law may also be stated thus: The *velocity of Brownian movement is uniform.* As Svedberg (*l.c.*) emphasizes, this is of great importance because it compels the conclusion that the forces causing Brownian movement cannot, for example, be elastic in type. The period of elastic vibrations, like that of small oscillations of the pendulum, is *independent* of the amplitude or path length.

This law may be experimentally tested in different ways. The path of a vibrating particle may be divided by the time. If the law is valid the quotient must be constant. Or the amplitude which varies with the temperature and the time of vibration may be measured at different temperatures. The most convenient method, perhaps, is to compare the movements of equally sized particles in liquids of different viscosities and see if the quotient $\frac{\text{Path}}{\text{Time}}$ is constant, for, as will be developed more fully later (page 202), their velocity is markedly dependent on the viscosity of the dispersion means. The Svedberg (*l.c.*, 1906) has used this last method.

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[1] The Svedberg, Z. f. Elektroch., **12**, 853, 909 (1909).

The following table shows how in colloid platinum the path length divided by the time yields a constant in different dispersion media. In judging the results the rather large experimental error must be kept in mind.

TABLE 30.—PROPORTIONALITY BETWEEN THE AMPLITUDE AND PERIOD OF VIBRATION IN THE BROWNIAN MOVEMENT OF COLLOID PLATINUM

(According to The Svedberg)

Dispersion means*	Amplitude, $2A$ in μ	Period of vibration, $2t$ in sec.	Quotient $\frac{2A}{t}$ = const.
Acetone	6.2	0.032	194(18°)
Ethyl acetate	3.9	0.028	139(19°)
Amyl acetate	2.9	0.026	112(18°)
Water	2.1	0.013	162(20°)
Normal propyl alcohol	1.3	0.009	145(20°)

*That the temperature varied between 18° and 20° must be kept in mind.

5. Influence of the Specific Surface of the Particles.—Not until the diameter is reduced below a certain limit, which Wiener (*l.c.*) judged to be about 3–5μ, do dispersed particles begin to show a noticeable Brownian movement. The rapidity of movement increases with decrease in the size of the particles if all other conditions remain constant. The following figures, taken from F. M. Exner (*l.c.*), illustrate the dependence at constant temperature (23°) of velocity upon size in the case of gutta-percha particles.

TABLE 31.—DEPENDENCE OF BROWNIAN MOVEMENT ON SIZE OF PARTICLES

(According to F. M. Exner)

Diameter of particles in μ	Velocity of particles in μ per sec.
1.3	2.7
0.9	3.3
0.4	3.8

The average absolute velocity of *colloid* particles, according to The Svedberg (*l.c.*) is about

$$0.02 \text{ to } 0.04 \ \frac{\text{cm.}}{\text{sec.}}$$

or

$$200 \text{ to } 400 \ \frac{\mu}{\text{sec.}}$$

in other words, about 100 times that of microscopic coarsely dispersed particles. There exist, of course, all possible transitions between these two extremes. It would be of interest to make an extended study of this function of velocity × degree of dispersion.

6. Influence of Concentration of Dispersoid.—The velocity depends on the number of particles in the unit volume. R. Zsigmondy[1] found "the particles to influence each other and the vigor of their movement to be decreased by dilution of the gold particles." A quantitative study of this important relation is still lacking.

7. Influence of Viscosity of Dispersion Medium.—As easily foreseen, the greater the viscosity, the slower the movement. The Svedberg (*l.c.*) studied this relation in colloid solutions, finding that the relation of the average velocity or path length to the viscosity of the dispersion medium may be represented by an equilateral hyperbola. In other words, the relation

$$A\eta = \text{const.},$$

holds, in which A represents the amplitude and η the viscosity of the dispersion medium. *The path length is inversely proportional to the viscosity of the dispersion medium.* The range over which this law is valid is indicated in Table 32.

TABLE 32.—DEPENDENCE OF PATH LENGTH OF BROWNIAN MOVEMENT OF COLLOID PLATINUM PARTICLES ON VISCOSITY OF DISPERSION MEDIUM

(According to The Svedberg)

Dispersion medium	Path length $2A$ in μ	Viscosity in c.g.s. units η 10^3	$2A\eta$ = const.
Acetone	6.2	3.2	19.8
Ethyl acetate	4.0	4.6	18.4
Amyl acetate	3.0	5.9	17.7
Water	2.2	10.2	22.4
Normal propyl alcohol	1.4	22.6	31.6
p-Isobutyl alcohol	1.2	39.3	47.3

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[1] R. Zsigmondy, Z. Erkenntnis d. Kolloide, 111 (Jena, 1905).

As can be seen, the product $2A\eta$ increases when the higher viscosities are attained, though here the measurement of the path length is very difficult. Table 33 brings out the same facts from a study of electrically prepared calcium organosols. The approximate changes in path length are again shown.

TABLE 33.—DEPENDENCE OF PATH LENGTH OF BROWNIAN MEVEMENT OF COLLOID CALCIUM PARTICLES ON VISCOSITY OF DISPERSION MEDIUM

(According to The Svedberg)

Dispersion medium	Path length $2A$ in μ	Viscosity in c.g.s. units $\eta.10^3$	$2A.\eta$
Ethyl ether	8.0–9.0	2.4	19.2–21.6
Ethyl acetate	4.0–5.0	4.7	18.8–23.5
Chloroform	2.0–3.0	5.8	11.6–17.4
Ethyl alcohol	0.5–2.0	12.6	6.35–25.4
Isobutyl alcohol	Immeasurably small	40.0	?

8. Influence of Temperature.—Rising temperature accelerates Brownian movement, but, it must be remembered, this also decreases the viscosity of the dispersion medium. Thus gutta-percha particles, 0.9μ in diameter, have an average velocity of 3.2μ per second at 20°, while at 71° they have one of 5.1μ per second (F. M. Exner, *l.c.*). M. Seddig (*l.c.*) has investigated the influence of temperature more exactly. He finds that the amplitude or movement of the particles, after a definite time, is dependent on the temperature, according to the formula:

$$A = k.\sqrt{\frac{T}{\eta}}$$

in which A is the amplitude, T the absolute temperature and η the viscosity.[1] The values as determined average 6 percent above the calculated, but this difference is plausibly explained as due to the disturbing influence of heat upon the photographic process employed to record the movements. This explains why all the deviations occurred *in the same direction*. For details Table 34 should be studied.

The observations F. M. Exner suffice to prove the validity of

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[1] Strictly speaking, Seddig investigated the validity of the above formula indirectly, in that he determined the ratio of the amplitudes to each other at different temperatures and not the change in their absolute value with the temperature.

TABLE 34.—DEPENDENCE OF BROWNIAN MOVEMENT ON TEMPERATURE (According to M. Seddig)[1]

Temperature of observation		Viscosity of dispersion medium		Relation of displacements		Deviation in per cent
t_1	t_2	at t_1	at t_2	at t_1 and t_2		
				Observed	Calculated	
20.0	90.0	0.0101	0.0032	2.07	1.977	+4.7
20.0	90.0	0.0101	0.0032	2.08	1.977	+5.2
20.0	72.5	0.0101	0.00392	1.9	1.743	+9.0
17.0	90.0	0.01106	0.0032	2.20	2.080	+5.8
17.0	72.5	0.01106	0.00392	1.99	1.833	+8.6
17.0	90.0	0.01106	0.0032	2.18	2.080	+4.8
10.0	90.0	0.01309	0.0032	2.37	2.290	+3.5
17.0	90.0	0.01106	0.0032	2.21	2.080	+6.3
17.0	90.0	0.01106	0.0032	2.19	2.080	+5.29
12.9	90.0	0.01258	0.0032	2.32	2.234	+3.9
15.0	90.0	0.0113	0.0032	2.22	2.110	+5.2
12.9	90.0	0.01258	0.0032	2.39	2.234	+6.7
5.5	90.0	0.01494	0.0032	2.64	2.463	+7.2

this function as J. Perrin (*l.c.* 1910, page 269) has pointed out, for the value 1.6, which expresses the ratio of the path lengths, $\frac{A_2}{A_1}$ at a temperature increase from 20° to 71°, almost equals 1.7, the square root of the expression

$$\frac{T_2.\eta_1}{T_1.\eta_2} = \frac{342 \times 0.010}{293 \times 0.004},$$

which is clearly only an algebraic transformation of the above equation. If this is given the form:

$$A^2 = k_1.\frac{T}{\eta},$$

it is seen that *the square of the path length* ***is directly proportional*** *to the ratio of the absolute temperature* ***and the viscosity.*** If the influence of the latter is eliminated by using Svedberg's law ($A\eta = k$), the result is:

$$A_2\eta = A.A\eta = k_1T;\ A\eta = \text{const.};\ A = k_2.T,$$

in other words, the ***path length is directly proportional to the absolute temperature when the viscosity is constant.***

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[1] The figures used in this table were collected by W. Mecklenburg (*l.c.*, page 77).

9. Influence of Added Substances.—Even the earlier authors knew that small amounts of electrolytes greatly reduce or even stop Brownian movement. As a rule, this cessation is closely connected with a clumping into larger complexes, a process usually ending in a precipitation or coagulation of the system. Hence it has been assumed [see Svedberg (*l.c.*, 1907)] that the addition of electrolytes retards Brownian movement only because it causes an *increase in the size* of the vibrating particles. Though this view may be largely correct, recent observations have shown that retardation of Brownian movement may occur even when there is no clumping, and what is more important, it may even be *accelerated* on adding electrolytes. Thus V. Henri (*l.c.*) found the movement of the rubber globules in latex to be reduced by half on adding N/10 NaOH, and to one-ninth the original rate when N/32 HCl was added, even though no clumping could be detected. While the path length normally averaged 0.62μ per $\frac{1}{20}$ second, it was reduced to 0.31μ in the alkaline medium and to but 0.07μ in the acid. The normal path of these globules is shown in Fig. 34. The path in an alkaline medium is shown in Fig. 35; that in an acid one in Fig. 36. Lecoq[1] observed the addition of electrolytes distinctly to *increase* the movement of colloid metallic arsenic, but unfortunately he gives no details as to the substances and concentrations used.

The retardation might be explained by assuming that the added ions are absorbed by the latex globules causing an enlargement of the particles and a slowing of their movement through the hydrate envelopes added in this way. But this explanation does not harmonize with Lecoq's results, who found the rate to increase on adding electrolytes. Perhaps we need to consider other factors, such as electrical ones.

The retarding influence of certain non-electrolytes such as urea (Perrin, *l.c.*) on Brownian movement can easily be explained through the increase in viscosity of the dispersion medium which they bring about.

10. Influence of the Electrical Charge.—The investigations of The Svedberg and J. Perrin (discussed on p. 195) proved conclusively that the degree of movement of vibrating particles was independent of their electrical charges. These are the only investigations available on this point. Their repetition and extension to other dispersed particles is greatly needed. The following theoretical considerations make this complete independence appear strange. As familiarly known from the study of gaseous ions,[1] an electrically charged particle induces in its surroundings an electromagnetic field which opposes its movement. One would therefore assume, if any effect of the particles upon each other were excluded, that the spontaneous movement would decrease as the electric charge increased and that when the charge is zero, in other words, at the iso-electric point, motion would be greatest. As a matter of fact, traces of electrolytes when adsorbed by the vibrating particles may retard their movement through changes in their charges in either a positive or a negative sense and it is therefore not impossible that the phenomena observed by Henri and Lecoq may be associated with such charging and discharging.

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[1] Lecoq, Compt. Rend., **150**, 700 (1910).

Perhaps future investigators, using more exact methods than could Svedberg, will prove the *fundamental* though not the *functional* independence of Brownian movement of the size of the charge of the particles.

11. Influence of Gravity on the Distribution of Oscillatory Particles.—J. Perrin (*l.c.*, 1910), in part with Chaudesaigues and Dabrowski has studied the *distribution* of the dispersed particles in fine mastic dispersoids when left to the influence of gravity. The problem is not one of simple sedimentation in the ordinary sense of the word, for these systems are so highly disperse (the particles having a diameter of 0.5-0.7μ) that a settling out of the disperse phase can occur only after a very long time, if at all. The investigation dealt rather with the stratification of particles showing Brownian movement. Such stratification is evidently the result of a force (gravity) acting in one direction on the Brownian movement.[2] On *a priori* grounds we would expect that the greater density[3] or "excess weight" possessed by some of the particles would add to the previously irregular movement a component directed downwards, thus changing the previously uniform distribution of the particles into an uneven one in which a more concentrated layer appears at the bottom.

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[1] See J. J. Thomson, Conduction of Electricity through Gases, Cambridge, 1903.

[2] Analogous stratifications are to be expected under the influence of other unidirectional forces, as electrical or magnetic.

[3] In the case of specifically *lighter* particles we would except similar differences in distribution to result in the formation of a "scum."

Perrin's investigations were not carried out in tall cylinders as one might be inclined to expect, but in small microscopic columns of liquid not more than 100μ high. The arrangement of the apparatus is shown in Fig. 44. The different levels in the liquid columns were reached and studied by simply raising or lowering the objective. The particles in the different *optical* sections were counted either photographically or by a special process[1] and their number in the different sections compared.[2] Figs. 45 and 46 are photographs obtained by Perrin showing the distribution of gutta-percha particles when such methods are used.

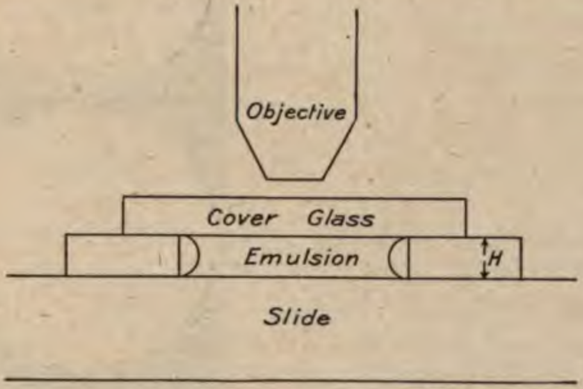

FIG. 44.—Arrangement for determining the distribution of particles in a mastic dispersoid. (According to *J. Perrin.*)

These measurements yielded the important law: *The concentration of the disperse phase increases in geometric progression with the algebraic decrease in the height of the level.* Symbolically expressed this would be:

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[1] This consisted of so narrowing the field of vision by a diaphragm that only a few (5–6) particles were visible at a time. They could then be easily counted. The average of a large number of such readings (Perrin made thousands in some cases) yields with sufficient exactness, the number of particles in each of the layers.

[2] Two other methods which seem to offer advantages and which might be used are the following: Metallic colloids are produced in molten paraffin and poured into heated metallic rings or tubes. After standing some time, the paraffin is solidified *as quickly as possible*, as by plunging into liquid air. Sections are then cut with an ordinary microtome and the particles in each counted ultramicroscopically. A yet simpler method would consist in filling a burette with a suitable dispersoid and keeping this for some time at constant temperature. Different layers could then be carefully drawn off and their content of the disperse phase be determined either gravimetrically or by titration.

$$2.303 \log \frac{n_o}{n_h} = g.h$$

wherein n_o is the concentration (number of particles per unit volume) in the initial level o, n_h the concentration in the level h, g the constant of gravity, h the level and 2.303 the conversion factor of decadic to natural logarithms. The following table contains a compilation of several series of such experiments made by J. Perrin (*l.c.*, 1910).

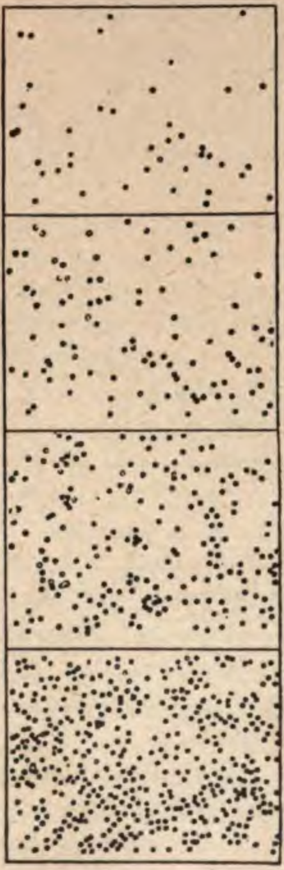

FIG. 45.

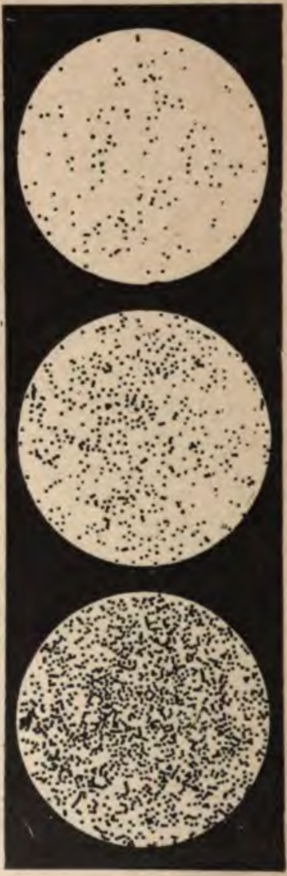

FIG. 46.

FIG. 45.—Distribution of oscillating gutta-percha particles under the influence of gravity. (According to *J. Perrin.*) (Diameter of field 0.6μ; four levels 10μ apart.)

FIG. 46.—Distribution of oscillating mastic particles under the influence of gravity. (According to *J. Perrin.*) (Diameter 1μ; three levels 12μ apart.)

TABLE 35.—DEPENDENCE OF CONCENTRATION ON LEVEL OF LAYER IN SUSPENSIONS

(According to J. Perrin)

Gutta-percha Suspensions, Diameter of particles						Mastic Suspensions, Diameter of particles					
0.28μ			0.24μ			about 6μ			about 1μ		
Height of level	Observed concentration	Calculated concentration	Height of level	Observed concentration	Calculated concentration	Height of level	Observed concentration	Calculated concentration	Height of level	Observed concentration	Calculated concentration
100μ	100	100	90μ	12.0	11.1	35μ	10	9.4	24μ	305	280
75	116	119	60	22.6	23.0	25	22	21.0	18	530	528
50	146	142	30	47.0	48.0	15	43	45.0	12	940	995
25	170	169	0	100.0	100.0	5	100	100.0	6	1880	1880
0	200	201	....	....	....	....	....	......	...	....	. .

12. Validity of Stokes' Law for Highly Dispersed Particles.—G. Stokes in 1850 formulated a law for the motion of small spheres in a viscous liquid, which has gradually become famous. If we call F the force acting on the spherical particle, r its radius, v its velocity and η the viscosity coefficient of the liquid, the formula is:

$$F = 6\pi\eta r v$$

in other words the force required to maintain the velocity v is proportional to the latter, as well as to the radius and the coefficient of viscosity. If only gravity acts on the particle, we have

$$F = \frac{4\pi}{3} r^3 (D - d) g$$

where D is the density of the particle, d that of the liquid, and g the gravity constant. By introducing this value for F in the formula and transforming, we obtain the following expression for the velocity of a small sphere sinking (or rising) in a liquid

$$v = \frac{2}{9} \frac{D - d}{\eta} g r^2$$

Everything else being constant, *the velocity of a small sphere falling in a liquid is therefore proportional to the square of its radius.* Stokes employed the formula to calculate the rate of sinking of drops of water forming clouds, etc. What interests us is whether this law also holds when the degree of dispersion is very high as in dispersoids showing Brownian movements (J. Perrin,[1] J. Duclaux[2]).

J. Perrin was able to show that the law is still valid for particles with a radius of 0.14 to 0.45μ, in other words, for such as approach the maximum diameter (1μ) of colloid particles. He measured the *sizes of the particles* of his suspensions, first, by calculating their sedimentation velocities from Stokes' law, second, by counting the particles in a known volume containing a known amount of disperse phase, and thirdly, by a micrometric method (for the details of which see his paper of 1910). The three methods give results which agree closely with one another as evidenced in Table 36.

Table 36.—Determination of Sizes of Particles by Different Methods to Test Applicability of Stokes' Law to Highly Dispersed Systems

(According to J. Perrin)

By counting	According to Stoke's law	Micrometrically
0.46μ	0.45μ	0.45·5μ
0.30	0.29	0.30
0.212	0.212	....
0.14	0.12	....

Whether this law holds for systems of still higher degrees of dispersion has not yet been determined, though it is already applied with remarkable results, not only to the theory of *molecularly dispersed solutions* (see for example W. R. Bousfield[3]) but to the migration phenomena of gaseous ions.[4]

13. Kinetic Theory of Brownian Movement.—As mentioned before, the sources of energy for Brownian movement must be sought in some very general mechanical forces resident *within* fluid or gaseous dispersoids. In harmony with the old accepted and widespread kinetic views it was to be expected that Brownian movement would sooner or later be regarded as a direct result of the supposed collisions between the molecules of the dispersion medium. As a matter of fact, the early authors (Chr. Wiener, G. Gouy, etc.), saw in this its only possible explanation. Recently, A. Einstein[1] and M. von Smoluchowski,[2] in some exceedingly important papers on molecular physics have developed by somewhat different methods a theory of Brownian movement resulting in two almost identical formulæ. Their fundamental equation governing the kinetics of disperse systems reads:

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[1] J. Perrin, Compt. rend., **146**, 967 (1908); Kolloidch. Beih., *l.c.*, 1910.

[2] J. Duclaux, Compt. rend., **147**, 131 (1908).

[3] W. R. Bousfield, Z. f. phys. Chem., **53**, 270 (1905).

[4] See J. J. Thomson, Conduction of Electricity through Gases, Cambridge, 1903.

$$A = \sqrt{K.\frac{RT}{N}\cdot\frac{t}{\eta r}}$$

In this A is the average path length of the particle, K a constant, R the gas constant, T the absolute temperature, N the number of particles in a gram molecule of the disperse phase (Avogadro's constant), t the period of vibration, η the viscosity of the dispersion medium and r the radius of the spherical particle.

The formula of M. von Smoluchowski differs from that given above only in having the factor $\frac{64}{27} = 2.37$ preceding the root on the right side.

The derivation of the formula cannot be detailed here.[3] It will only be shown how well this equation, deduced theoretically, agrees with the experimental results of The Svedberg and J. Perrin. It should be emphasized that the two laws formulated by Svedberg concerning the uniformity of Brownian movement and its dependence on viscosity were discovered before he had any knowledge of the Einstein-Smoluchowski formula.

Discussion of the equation leads to the following conclusions. If we assume all the factors in the equation to be constant, except the path length, period of vibration and viscosity, the equation becomes

$$A = K\sqrt{\frac{t}{\eta}} \text{ or } A^2 = K_1.\frac{t}{\eta}$$

The latter form states that not the path length but its square is directly proportional to the period of vibration and inversely proportional to the viscosity of the dispersion medium. Svedberg, however, found (see p. 202) the first power of the path length to be proportional to the period of vibration and inversely proportional to the viscosity. As a matter of fact, the above equation can be separated into two of the form:

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[1] A. Einstein, Ann. d. Physik. (4), 21, 17, 549 (1905); (4), 19, 371 (1906); Z. f. Elektrochem., 13, 41 (1907).

[2] M. von Smoluchowski, Ann. d. Physik. (4), 21, 756 (1906).

[3] See the original papers as well as the excellent pamphlet of W. Mecklenburg, Die experimentelle Grundlegung der Atomistik, Jena, 1910.

$$A^2 = k.\frac{t}{\eta} = \frac{A}{t} A\eta = k$$

If one of the factors, say $\frac{A}{t}$, is constant, as demanded by the kinetic gas theory (which assumes uniformity of average velocity of the gas molecules) and as Svedberg found it to be experimentally, then the other factor $A\eta$ must also be constant. Conversely, assuming the validity of Stokes' law, $A\eta$ becomes a constant, and therefore $\frac{A}{t}$ also. The formulas deduced from the kinetic theory therefore really cover the case in which both Svedberg laws are simultaneously active.

Experience therefore confirms the moleculo-kinetic deductions of the authors named.

With this equation it now becomes possible, conversely, to calculate the absolute value of Brownian movement when viscosity, size of particles, etc., are known. Svedberg (*l.c.*) and V. Henri (*l.c.*, 1908) have done this. Their calculated and observed results do not agree absolutely, but they are of the same order of magnitude and the deviations are all of about the same proportion. Undoubtedly the arbitrariness or inexactness of some of the constants used may therefore be held responsible. Table 37 shows the more important of these calculations.

TABLE 37.—CALCULATION OF PATH LENGTH OF COLLOID PLATINUM PARTICLES EXHIBITING BROWNIAN MOVEMENT, AFTER THE EINSTEIN-SMOLUCHOWSKI FORMULA
(According to The Svedberg)

Dispersion medium	$t \eta 10^3$ (in sec.)	A observed (in μ)	A calculated (in μ)	$\frac{A \text{ found}}{A \text{ calculated}}$
Acetone	0.032 2.3	3.1	0.71	4.4
Ethyl acetate	0.028 4.6	2.0	0.44	4.5
Amyl acetate	0.026 5.9	1.5	0.38	4.0
Water	0.013 10.2	1.1	0.20	5.5
n Propyl alcohol	0.009 22.6	0.7	1	6.4

With due allowance for the large experimental error, the value of the rotational movement of particles of disperse phase also agrees, as J. Perrin (*l.c.*) has shown, with that derived from the formula of A. Einstein. The law developed by J. Perrin governing the changes in concentration of a suspension at different levels (as discussed in §11) has also been deduced from considerations of the kinetics of gases. Only the constants of the formulas are different in the two cases. Thus while the density of the earth's atmosphere does not decrease by half until a height of about 6 kilometers is attained, the concentration of the dispersoids investigated by Perrin often fell off this amount when the difference between levels was only about 10μ.

It should also be pointed out that the constant N of the Einstein-Smoluchowski equation, in other words, the number of particles in a gram-molecule, which is of such great importance in various fields in physics and physical chemistry, can be calculated in different ways. The values thus obtained agree surprisingly well with those calculated from observations of the Brownian movement. Indeed it seems as though these methods as applied to submolecular dispersed systems yield the most exact figures of this fundamental value now obtainable. As this constitutes one of the brilliant achievements of colloid or dispersoid chemistry the following table taken from J. Perrin (*l.c.*, 1910) is given in full.

TABLE 38.—DETERMINATION OF THE NUMBER OF PARTICLES IN A GRAM-MOLECULE (AVOGADRO'S CONSTANT N) BY DIFFERENT METHODS

(According to J. Perrin)

Phenomenon Studied		$N. 10^{-22}$
Viscosity of gases	Average of volume in liquid state	> 45
	From the dielectric force of gases	< 200
	By using Van der Waal's equation	60
Brownian movement	From distribution of a uniform suspension	**70.5**
	From the average displacement in a given time	**71.5**
	From the average rotation in a given time	**65**
Diffusion of dissolved substances		40–90
Mobility of ions in water		60–150
Radiance of the sky		30–150
Direct measurements of atomic charge	Of droplets condensed upon ions	60–90
	Of ions attached to dust particles	**64**
Emissions of α corpuscles	Total charge emitted	62
	Time constant of radium	**70.5**
	Helium produced by radium	**71**
Energy of the Infra-red spectrum		60–80[1]

[1] See Perrin (1910) for details regarding other phenomena.

These brilliant results fill one with admiration for the remarkable fertility of the Einstein-Smoluchowski equation, especially when it is remembered how many still purely hypothetical factors enter into its composition. Nothing better illustrates the daring, we might say, of this train of thought than the remark of Perrin, to whom, with Svedberg, science owes most in this field, anent the theorem of the equality of the distribution of energy which is the nucleus of all kinetic deductions. "The word theorem should deceive no one, for it is full of hypotheses as is almost every theory of mathematical physics." It is safest, perhaps, to hold that the future will preserve but a *part* of our present kinetic notions and embody it into a more general, less conjectural theory. As a matter of fact, several of the laws governing Brownian movement may be deduced even *without* recourse to kinetic assumptions, as for example, the inverse proportionality of velocity to viscosity, from Stokes' law.[1] Possibly this purely inductive method will some day discover these same laws; in fact, consideration of the methods of science demands it, but when the day will come must remain a matter of opinion.

14. Determination of the "Molecular Weight" of Dispersed Particles from their Brownian Movement.—Since N can be calculated, the so-called "molecular weight" of dispersed particles may also be determined from the formula of Einstein and Smoluchowski. This can also be done from the logarithmic distribution equation governing concentration in different levels. J. Perrin[2] made such calculations and by this method found his gutta-percha particles to have a molecular weight of about 30,000,000,000. It must again be emphasized that these values cannot be compared with the molecular weights of molecularly dispersed particles. In the former, the *diameter* of the particles (or their volume) is under discussion, and this "molecular weight" becomes progressively less as the size of the particles decreases. The normal concept of molecular weight does not consider the size of the particles as at all variable, but deals simply with that single value which is observed at the maximum degree of dispersion. This obviously constitutes a fundamental distinction between the "molecular weights" of differently dispersed systems.

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[1] The influence of electrical energy upon Brownian movement as postulated on p. 205 cannot be deduced from kinetic considerations, but is an inductive conclusion. It appears in the Einstein-Smoluchowski equation as a factor analogous to the viscosity factor since the velocity would be approximately inversely proportional to the intensity of the induced field of force. Judging from the experimental results of Svedberg and Perrin these proportionality constants would, in many cases, have a very small value.

[2] J. Perrin, Compt. rend., **147**, 475 (1908).

§28. Diffusibility of Colloids

1. **General Remarks.**—When a quantity of the pure dispersion medium is poured on a molecular dispersion, with due precautions so as to avoid mixing, the dispersed phase wanders over into the dispersion medium until uniform distribution throughout both phases is attained. This phenomenon is known as *diffusion*. In trying to explain what has happened it is natural to think of the influence of Brownian movement. In the irregular, particularly in the forward, movements of small particles, as observed, for example, by Zsigmondy in colloid solutions, it is to be expected that an *accidental* wandering of the particles over into the pure dispersion medium must take place. But such accidental migration cannot wholly explain all diffusion, the laws of which A. Fick formulated in 1855. In order that Brownian movement may lead to diffusion, it must become directive in character toward the pure dispersion medium or toward the "more dilute" parts of any continuous system.

As a matter of fact, the existence of such a directive movement in diffusion until uniform distribution of the dispersed phase throughout the whole system is attained can be foreseen, when the relation between *degree of movement* and *concentration* of dispersed particles is called to mind. As noted above (p. 202), R. Zsigmondy observed *less* movement in dilute systems than in concentrated ones. Because of this, equilibrium cannot exist, so far as average velocity of particles is concerned, in a system consisting, say, of a colloid solution covered by a layer of the pure dispersion medium. In places of greater concentration, the particles will be moving faster than in those of a lower one. The sources of energy for Brownian movement, whatever they be, must therefore have different values in different parts of the system at the beginning of diffusion. But following the general laws of energy, equilibrium cannot be attained in a closed system until the energy intensities have the same value everywhere.[1] We need but call to mind the electrostatic charge on the surface of a metallic sphere. If the energy intensities in a "diffusion field" are not everywhere the same the system is unstable and changes must occur of a *directive* character leading, in the end, to an equalization of the intensities in the whole system. Thus, if only a local charge were present on the metallic sphere, currents would emanate from this to all other points on its surface. In the case of diffusion, a movement of the dispersed particles toward regions of lower concentration would have to occur until the average velocity of the particles was the same in all portions of the system. The average *absolute* value of the movement would therefore become progressively less until the minimum is attained at the end of diffusion. It is in keeping with this general notion that in the molecular dispersoids the diffusion coefficients (distances traversed in centimeters per day) are greater at higher concentrations than at lower ones.[1]

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[1] Wilh. Ostwald, Lehrb. d. allgem. Chem., 2 Aufl., 2, 35 (1903)

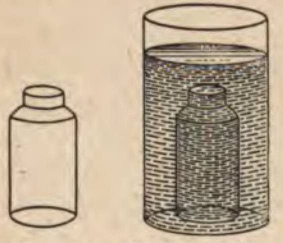
FIG. 47.—Apparatus for the study of diffusion as arranged by *Thomas Graham*.

The influence of concentration on the diffusion of a colloid has not yet been studied. The experimental difficulties besetting such a study will become clear in the following paragraphs.

Diffusion experiments have a special interest in colloid chemistry because its very foundations were built upon them by Th. Graham (1850–1862).

2. Experimental Study of Diffusion of Colloids.—The common method of determining the diffusion coefficient was originated by Th. Graham.[2] A wide-necked bottle is filled with the solution to be investigated and placed in a second vessel; the pure dispersion medium is then poured with special care[3] into the second vessel until it covers the inner bottle to a depth of several centimeters. Fig. 47 is an exact copy of the sketch from Graham's original work. After a given time, the amount of dissolved substance which has escaped from the inner vessel is determined. The relation of this to the time (at constant diffusion surface, temperature, etc.) is a measure of the velocity of diffusion. For a discussion of the more modern methods of using Graham's principle, as well as for the methods of calculating the absolute diffusion coefficients from the experimental data, the text-books of physics and physical chemistry should be consulted.[1]

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[1] The complicated diffusion phenomena observed in certain ionic dispersoids, as in hydrochloric acid, form exceptions to the general rule because electrochemical processes come into play. See Wilh. Ostwald, Lehrb. d. allg. Chem., 2 Aufl., **1**, 686 (1903).

[2] Th. Graham, Philos. Trans., 1–46, 805–836 (1850); 483–494 (1851), etc.; Liebig's Ann., **77**, 56, 129 (1851); **121**, 5, 29 (1862).

[3] To prevent mixing of the two liquids at the critical moment Graham used a pointed sponge from which to express the second liquid.

It is difficult in Graham's method to bring the two liquids into contact with each other without disturbing their surfaces. Slight differences in temperature, vibrations, etc., may, moreover, introduce great experimental errors. But Graham already knew a remedy for this. He found that the velocity of diffusion was not much influenced if the experiment was carried out in a not too highly concentrated agar-agar, gelatin or starch paste, instead of in pure water. Thus, when he placed in the diffusion cell a 2 percent agar solution containing 10 percent salt, and a pure agar solution of the same concentration in the outer vessel and allowed both to solidify, he found after 15 to 16 days that the latter contained 9.992 grams of diffused salt. Normal diffusion into pure water, after 14 days showed 9.999 grams, all other conditions, including temperature (10°), being constant. These findings have often been verified. Thus F. Voightländer[2] observed 0.72 percent sulphuric acid to diffuse the following distances into agar jellies of different concentrations after 1 hour.

Agar jelly, 1 percent = 8.5 mm.
2 percent = 7.8
4 percent = 7.0

The amounts that diffused were as follows:

Into agar jelly, 1 percent = 1.08 mg. SO_3
2 percent = 1.10
4 percent = 1.09

The absolute values for NaCl of the diffusion coefficients, $\frac{\text{amounts diffused in grams}}{\text{days}}$, are as follows:

Agar jelly, 1 percent = 1.04
2 percent = 1.03
3 percent = 1.03

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[1] See, for example, Wilh. Ostwald, Grundr. d. allg. Chem., 4 Aufl., 194, Leipzig, 1909; Wilh. Ostwald-Luther-Drucker, Hand- und Hilfsbuch, 3 Aufl.

[2] F. Voightländer, Z. f. physik. Chem., 3, 329 (1889).

G. Hüfner[1] and others obtained similar results. But it should again be emphasized that diffusion is thus independent of the presence of gels only when these are there in low concentrations. Marked retardations appear at higher concentrations as even H. de Vries[2] knew. Diffusion is also influenced, of course, when chemical or colloid-chemical changes, as precipitations, are produced in the gels by the diffusing substances.

A convenient arrangement for demonstrating diffusion has been described in the practical introduction on p. 9. Test tubes are half filled with colloid gels and the diffusing solution poured upon them. Figs. 2, 48 and 49 illustrate the results.

Disturbance of the diffusion surfaces may also be avoided by stretching over the inner vessel a suitable membrane through which the dissolved substances pass freely. Hydrophane plates (G. Hüfner, *l.c.*), filter papers (S. Exner, see below), parchment papers (The Svedberg, see below), etc., have been used for this purpose. Or, the diffusing substance may be placed directly in cells entirely made of such substances. But the membranes used must be completely permeable to the diffusing substance and must not affect it, as through adsorption, etc. §29 on dialysis should be studied in this connection.

3. Experimental Facts Regarding Diffusion of Colloids.—It follows from the relation between velocity of Brownian movement and size of particles discussed above that the velocities of colloid particles must be considerably less than those of molecularly or ionically dispersed ones. The compilation in Table 39 shows this clearly; additional facts regarding diffusion velocities are given below.

As is clearly evident, the diffusion coefficients of typical colloids average $\frac{1}{10}$ that of the slowly diffusing cane sugar and only $\frac{1}{100}$ that of the rapidly diffusing electrolytes such as acids and alkalies. The highly dispersed goldsol of The Svedberg which, for a colloid, diffuses exceptionally fast, takes an intermediate position. It should be remembered that the particles of the latter have a diameter of about $1\mu\mu$; in other words, this goldsol is on the boundary between molecular and colloid dispersoids.

Figs. 48 and 49 illustrate quantitatively the diffusion velocities

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[1] G. Hüfner, Z. f. physik. Chem., **27**, 227 (1898).

[2] H. de Vries, Fittica's Jahresber. d. Chem., **1**, 144 (1884)

TABLE 39.—DIFFUSION COEFFICIENTS OF DISPERSOIDS

Molecular and ionic dispersoids. Specific area $> 6 \times 10^7$		Colloids. Specific area about 6×10^7 to 6×10^5	
Nitric acid (Voightländer)	2.10 (20°)	Clupeinsulphate (Herzog)	0.074 (18°)
Sodium chloride (Voightländer)	1.04 (20°)	Pepsin (Herzog[3])	0.070 (18°)
Magnesium chloride (Voightländer)	0.77 (20°)	Rennin (Herzog)	0.066 (18°)
Copper sulphate (Landolt-Börnstein)	0.47 (17°)	Egg-albumin (Herzog)	0.059 (18°)
Urea (Scheffer[1])	0.81 (7.5°)	Albumin (Graham-Stefan)	0.063 (13°)
Cane sugar (Graham-Stefan[2])	0.31 (9°)	Caramel (Graham-Stefan)	0.047 (10°)
Mannite (Scheffer)	0.38 (10°)	Ovomucoid (Herzog)	0.044 (18°)
		Emulsin (Herzog)	0.036 (18°)
Gold hydrosol (The Svedberg[5])	0.27 (11.7°)	Invertin (Herzog)	0.033 (18°)
		Diphtheria-toxin (Arrhenius and Madsen[4])	0.014 (12°)
		Diphtheria-antitoxin (Arrhenius and (Madsen)	0.0015 (12°)
		Tetanolysin (Arrhenius Madsen)	0.037 (12°)
		Antitetanolysin (Arrhenius and Madsen)	0.0021 (12°)

of various dispersoids. They show what has happened after about 3 day's diffusion into solid 1.5 percent agar at 20°. In Fig. 49 the supernatant liquids out of which diffusion has occurred have been poured off so that the diffusion phenomena may show up more clearly. To the left in this figure are found molecular dispersoids, to the right, typical colloids. The tubes are arranged, from left to right, according to the lengths of the diffusion paths.[6] The picric acid, cobalt nitrate and eosin of tubes 1, 2, and 3 have wandered almost to the bottom of the agar column; benzo-purpurin and congo red on the extreme right have scarcely moved. The dyes lying between these, show intermediate degrees of diffusibility.[7] Fig. 48 shows the results, after 8 days, of experiments on the diffusion of typical colloids (hydrosols of silver, gold, antimony sulphide, arsenic sulphide and iron hydroxide). The *sharpness of the boundary line* between the diffusing substance and the gel should be noted. It is sharp in the case of typical colloids; but badly marked in that of the molecular dispersoids and systems of intermediate degrees of dispersion.

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[1] G. Scheffer, Z. f. physik. Chem., **2**, 390 (1888).

[2] Graham-Stefan, Sitz. Ber. Ak. Wien, **77**, II, 161 (1879).

[3] R. O. Herzog (and H. Kasarnowski) Koll.-Zeitschr., **2**, 1 (1907); **3**, 83 (1908); Bioch. Zeitschr., **11**, 172 (1908).

[4] S. Arrhenius and Th. Madsen, Immunochemie, 16, Leipzig, 1907.

[5] The Svedberg Z. f. physik. Chem., **67**, 107 (1909).

[6] The gradation is not as clearly shown in the photograph as it actually appears since the different (mostly 0.1 percent) solutions have different colors. A photographic plate does not bring this out.

[7] Regarding the diffusibility of dyes see L. Vignon, Compt. rend., **150**, 690 (1910).

4. Influence of Degree of Dispersion on Diffusion Velocity.—The diffusibility of a disperse phase is intimately connected with its degree of dispersion as shown in Table 39. Among molecularly dispersed substances, ions or electrolytes migrate most rapidly. Substances of higher molecular weight, or, more correctly, of greater atomic aggregation, follow. Last in the list, stand the colloids. This dependence of diffusion velocity on the size of the particles is of great interest. Of special importance is the possibility of procuring *one and the same substance* in different degrees of dispersion and therefore possessed of different degrees of diffu-

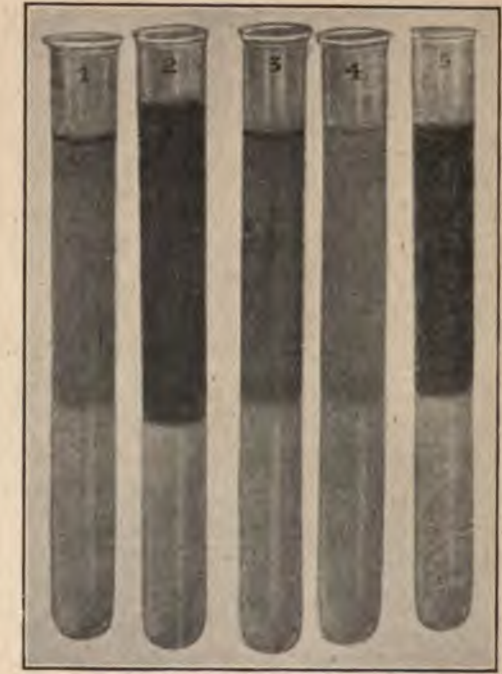

FIG. 48.—Diffusion of colloids into 2 percent agar-agar at the end of a week. 1. Gold hydrosol; 2. silver solution (*Credé*); 3. antimony sulphide solution; 4. arsenic trisulphide solution; 5. iron hydroxide solution.

sibility. S. E. Linder and H. Picton[1] were able to prepare the following four systems of arsenic trisulphide in water:

αAs_2S_3; particles microscopically visible, non-diffusible (coarse suspensions),

βAs_2S_3; microscopically homogeneous, non-diffusible,

γAs_2S_3; diffusible, but unfilterable through porcelain cups,

δAs_2S_3; diffusible and filterable.

After Wo. Ostwald[2] had repeatedly emphasized the great theoretical interest attaching itself to a systematic and quantitative investigation of the relations between diffusibility (and other properties) and degree of dispersion, The Svedberg,[3] in the prosecution of his experimental study of the Einstein-Smoluchowski formula (see above), attacked the problem. He determined the diffusion velocities of different gold hydrosols by pouring these into parchment cells having different porosities. His results are given in Table 40:

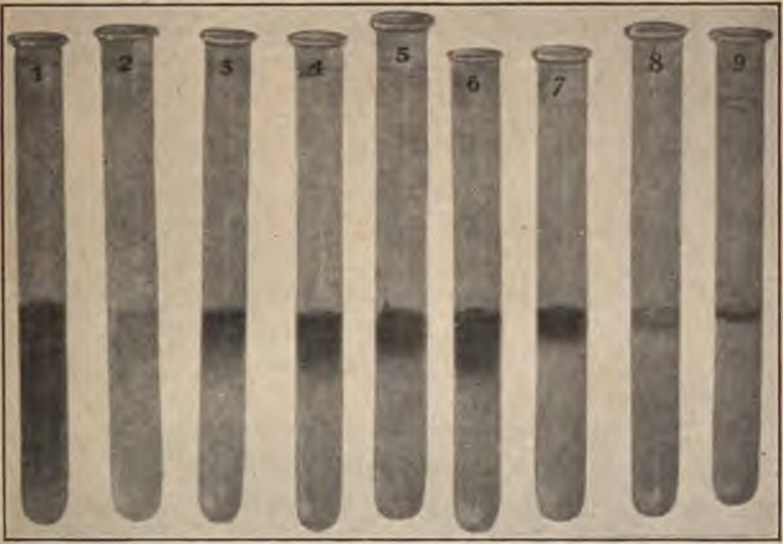

FIG. 49.—Diffusion into a 2 percent agar-agar at the end of three days. 1, Picric acid; 2, cobalt nitrate; 3, 0.1 percent eosin; 4, 0.1 percent ponceau R. R. R.; 5, 0.1 percent new fuchsin O; 6, 0.1 percent vesuvin; 7, 0.1 percent safranin G.; 8, 0.1 percent benzopurpurin; 9, 0.1 percent congo red.

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[1] S. E. Linder and H. Picton, Trans. Chem. Soc., Lond., **61**, 114, 137, 148 (1892); **67**, 63 (1895); **71**, 568 (1897); **87**, 1906 (1905).

[2] See, for example, Wo. Ostwald, Koll.-Zeitschr., **1**, 298 (1907).

[3] The Svedberg, Z. f. physik. Chem., **67**, 105 (1909).

TABLE 40.—DEPENDENCE OF DIFFUSION VELOCITY ON SIZE OF PARTICLES IN GOLDSOLS

(According to The Svedberg)

Size of particles in $\mu\mu$	Concentration of inner liquid in normality	Concentration of outer liquid in normality	Relation of concentration to each other
14	$1.5 \ 10^{-4}$	$1.5 \ 10^{-6}$	100
20–30	$1.5 \ 10^{-4}$	$1.3 \ 10^{-7}$	1200

The gold content was determined colorimetrically. The reciprocal values of the concentration *ratios* are measures of the diffusion velocity. In other words, $D_1 = k_1 . 1/100$, when D is the diffusion coefficient and k_1 the proportionality constant. Similarly, $D_2 = k_2 1/1200$. When the ratio of these diffusion coefficients is compared with the size of the particles (taking the latter to average respectively 2.5 and 25μ) we observe, since $\frac{2.5}{25} \backsim \frac{100}{1200}$ that *the diffusion velocity is approximately inversely proportional to the size of the particles, or* $D.r =$ *constant.*

True it is, that we are basing these conclusions on studies involving but two degrees of dispersion. An investigation covering a wider range would be of great interest.

Finally, it should be mentioned that S. Exner[1] found coarse suspensions, such as clay silt, to show a distinct though slow diffusion. But whether pure dispersions made up of particles larger than 5μ and therefore free from Brownian movements are really capable of true diffusion appears doubtful (see below, p. 224).

5. Theory of Colloid Diffusion.—The close relation between Brownian movement and diffusion was mentioned at the beginning of this paragraph. It seems natural, therefore, that the moleculo-kinetic considerations of A. Einstein and M. von Smoluchowski,[2] which proved so fruitful in the mathematical discussion of Brownian movement, should lead to similarly important results when applied to diffusion. For example, the inverse proportion between size of particles and diffusion velocity is deducible from the equations of Einstein and von Smoluchowski. For the diffusion coefficient they developed the equation:

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r}.$$

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[1] S. Exner, Sitz. Ak. Wiss., Wien, **56**, 116 (1867).

[2] According to von Smoluchowski the right side of the equation contains the factor 2.03.

The symbols have again the meaning indicated on p. 211, r representing the radius of the particles. If dispersion medium, temperature, internal friction, etc., are constant, the diffusion coefficients of two dispersed phases bear the following relation to each other:

$$\frac{D_1}{D_2} = \frac{r_2}{r_1},$$

in other words, they correspond to Svedberg's experimental findings.

This relation has much in common with the equation which expresses the connection between the diffusion of molecular dispersoids and their molecular weight. The relation:

$$D.\sqrt{m} = \text{constant}$$

has been established by S. Exner, for gases, and by L. L. Öholm[1] for (theoretically) infinitely dilute solutions of non-electrolytes. In this equation m is the molecular weight.

Conversely, with the laws of Exner-Öholm and Einstein-Smoluchowski, we may calculate the size of the particles as well as their molecular weight. In this way R. O. Herzog (*l.c.*) found an approximate agreement between the "molecular weights" of ovalbumin, hemoglobin, etc., thus calculated; and the figures obtained by other methods. For the values for toxins, etc., as calculated by Svante Arrhenius and Th. Madsen (*l.c.*), control measurements are not yet available. The same objections may be raised against all these calculations which were raised in discussing the determination of the molecular weight of colloid systems by freezing point, boiling point and vapor pressure methods.

The calculations by R. O. Herzog and The Svedberg (*l.c.*) of the size of the particles by the formula of Einstein-Smoluchowski are less open to objection. Herzog, on this basis, calculated the size of the particles of ovalbumin to be $2.86\mu\mu$. This figure about corresponds to the *higher* dispersion values obtaining within colloid systems, and therefore agrees well with the general fact that the colloid properties of the albumins place them near the molecularly dispersed systems. Svedberg calculated, in a reverse manner, the size of the particles of the highly dispersed gold solution of R. Zsigmondy, the particles of which, according to Zsigmondy, had a diameter of 1 to $4\mu\mu$. He obtained, by Einstein's formula, $0.94\mu\mu$, and by Smoluchowski's $2.16\mu\mu$. The calculated diameter of the particles of molecularly dispersed systems also agrees well with the values obtained by other methods.

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[1] L. L. Öholm, Z. f. physik. Chem., **70**, 378 (1910); this also includes the earlier literature.

6. Effect of Added Substances on Colloid Diffusion. Spurious Diffusion of Colloids.—The effects upon diffusion of adding different substances are so complicated, even in molecular dispersoids, that general laws governing them have not been formulated.[1] It is to be expected that these relations will be still more complicated when phases having different degrees of dispersion are mixed. The more important phenomena observed when colloid systems are mixed with molecularly dispersed ones are the following:

The effect of electrolytes on the diffusion velocity of colloids may be discussed under two headings—the *electrolyte may be added to the diffusing substance*, or the diffusion of the colloid may be permitted to occur *into the solution of an electrolyte*. In either case, different results may be expected, depending on whether the electrolyte does *not* affect the degree of dispersion of the colloid (which is exceptional) or whether it increases or decreases it. Both an increase and a decrease in the degree of dispersion on adding substances from without have been described in the literature. An illustration of the latter is found in the common and well-known effects of electrolytes on colloids (aggregation, coagulation); an illustration of the former, in the phenomena of peptization.

The *inhibiting effect* of added substances on diffusion has been studied by E. von Regéczy.[2] He found pure albumin when placed in parchment-paper tubes to diffuse out of these in the course of 12 hours in sufficient amount to impart a decided albumin reaction to the outer liquid. But when some solid NaCl was previously added to the albumin, no trace came out. S. E. Linder and H. Picton (*l.c.*, 1905) noted a similar behavior in an inorganic colloid, arsenic trisulphide. They allowed a highly dispersed arsenic trisulphidesol to diffuse, on the one hand, into water, on the other, into an NH_4Cl solution, so dilute that it caused *no* visible coagulation. Their results are given in the following table:

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[1] See, for example, Wilh. Ostwald, Lehrb. d. allg. Chem., 2 Aufl., 674, Leipzig, 1903.
[2] E. von Regéczy, Pflüger's Arch., **34**, 431 (1884).

TABLE 41.—DIFFUSION OF As_2S_3 SOL INTO PURE WATER AND INTO NH_4Cl SOLUTION

(According to S. E. Linder and H. Picton)

Time	Diffused amounts in percent of the inner fluid	
	Into pure water	Into NH_4Cl
24 hours	10 percent	1 percent
48	14	..
72	..	3
96	23	..

An antimony sulphidesol gave similar results when permitted to diffuse into water and into a solution of tartar emetic.

An example of how the addition of an electrolyte may *favor* diffusion of a colloid is found in Th. Graham's paper (*l.c.*). He observed egg albumin, which in its natural state is slightly alkaline and diffuses but slowly, to diffuse more rapidly if it is carefully neutralized with acetic acid. While after a week but 0.63 gm. of native (alkaline) albumin diffused out, 0.94 gm., in other words 30 percent more, came out when the albumin was neutralized. The neutralization increases the degree of dispersion, as proved by the observations of Wo. Pauli and others (see p. 173), who found neutral albumin to increase the viscosity of water less than acidified albumin.

H. Picton (*l.c.*, 1892) made similar observations on suspensoids of antimony trisulphide. He found this to diffuse rapidly when still contaminated with the tartar emetic from which it was prepared. Whether the electrolyte serves to increase the degree of dispersion in this case remains a matter of question, though such an influence on suspensoids has been observed. It is more reasonable to assume that the electrolytes in their rapid diffusion simply drag the colloid particles along with them, a view held by H. Picton himself; or that the movements of the liquid, caused by the diffusion of the electrolytes, set up currents which bring about the observed results.

The interesting experiments of W. R. Whitney and J. Blake[1] on the *great velocity of diffusion* of goldsols, produced by reducing ether solutions of gold chloride by means of acetylene, must, no tion of R. Zsigmondy, the particles of whi [illegible] concentrated their mondy, had a diameter of 1 to $4\mu\mu$. He o [illegible] cylinder by formula, $0.94\mu\mu$, and by Smoluchowski's [illegible] water upon it, diameter of the particles of molecularly [illegible] spontaneous upward agrees well with the values obtained by o [illegible] increase in the

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[1] W. R. Whitney and J. Blake, Journ. Amer. Chem. Soc., **26**, 1339 (1904).

6. Effect of Added Substances on Coll [illegible] velocities varied **Diffusion of Colloids.**—The effects upon [illegible] it is recalled that ent substances are so complicated, even [illegible] diffusing sulphuric that general laws governing them have [illegible] percent agar while the is to be expected that these relations will [illegible] coefficient of only when phases having different degree [illegible] acid on the same The more important phenomena observ [illegible] the experiments of mixed with molecularly dispersed on [illegible] of a colloid phase.

The effect of electrolytes on the [illegible] dispersoids present may be discussed under two head [illegible] (apparent) diffusion *added to the diffusing substance*, or th [illegible] of H. Picton. More be permitted to occur *into the soluti* [illegible] coated with gas through case, different results may be expec [illegible] was subjected and this electrolyte does *not* affect the deg [illegible] experiments could easily (which is exceptional) or wheth [illegible] an explanation. Both an increase and a decrease i [illegible] upon the diffusion of col- ing substances from without hav [illegible] they are permitted to diffuse An illustration of the latter is [illegible] von Wittich[1] found, as far known effects of electrolytes on [illegible] easily into a salt solution an illustration of the former, i [illegible] limits, *the diffusion is the*

The *inhibiting effect* of add [illegible] *of the salt.* E. von Regéczy studied by E. von Regéczy.[2] [illegible] have since studied this phenom- in parchment-paper tubes to [illegible] is the source of Table 42. 12 hours in sufficient amou [illegible] the amounts of diffused albumin in- action to the outer liquid. [illegible] concentrations of NaCl, but in the in- viously added to the album [illegible] 0.56 to 1.30 percent, a region of and H. Picton (*l.c.*, 1905) n [illegible] What follows will show that this colloid, arsenic trisulphid [illegible] experimental error. arsenic trisulphidesol to [illegible] phenomena,[3] we need but remember that the other, into an NH_4C [illegible] strongly hydrated, in other words, visible coagulation. Th [illegible] solutions than in pure water. We may table: [illegible] the free, dispersed albumin particles wander into the strongly hydrating *dispersion medium* just as the liquid wanders into the solid colloid to make it "swell." A sufficiently marked hydration of the dispersed particles must separate them from one another.

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[1] See, for example, Wilh. O [illegible] Arch. f. Physiol., 286 (1856).

[2] E. von Regéczy, Pflüger [illegible] Arch. f. Physiol., 20, 102 (1904).

[illegible] 3, 11 (1908).

TABLE 42.—DIFFUSION OF SERUM ALBUMIN INTO NaCl SOLUTIONS
(According to M. Oker-Blom)

Concentration of NaCl in the outer liquid	Amount of albumin, in grams, diffused after 24 hours
0	0.053
about 0.28 percent	0.053
0.56	0.052
0.74	0.052
0.93	0.050
1.30	0.052
1.48	0.058
1.86	0.060
2.38	0.079

At the present time, we can only guess at what may be the influence of several colloids upon each other when they are mixed, and how they must affect each other's diffusion velocity.

The influence of concentration and of temperature on the diffusion of colloids has not yet been studied. Judging from the findings of Th. Graham (*l.c.*), the rate of increase in diffusion velocity of egg albumin with the temperature is about as great as that of molecularly dispersed systems under the same circumstances, but exact figures on the subject are still wanting.

§29. Dialysis of Colloid Systems

1. General Remarks.—The impeding effect of concentrated gels or membranes upon free diffusion was touched upon above. While ordinary electrolytes pass through parchment-paper membranes almost as rapidly as though they were not there, albumin and gum arabic cannot penetrate them. Th. Graham, who first investigated this phenomenon, called it *dialysis* (1861). He noted that all substances which, when allowed to diffuse in the open, do so only slowly or not at all are also restrained by parchment membranes. On the other hand, those which diffuse rapidly are not markedly checked in their movement through the presence of membranes. This difference in behavior of "dissolved" substances toward parchment paper formed the basis of the whole concept of the colloids. Substances which do *not* dialyze (or pass through parchment paper) Graham called colloids, those which *do*, crystalloids. The latter systems are today known as "molecular dispersoids."

One can readily accomplish a separation of the different classes of dispersed systems by dialysis. As a matter of fact, Graham called his fundamental work "Liquid Diffusion Applied to *Analysis*." By using a constant type of membrane, systems of unknown degrees of dispersion may be classified into such as dialyze and such as do not (see the practical introduction). When, by any method whatsoever, coarsely dispersed systems have been excluded, dialysis offers a convenient method of distinguishing between the colloid and molecularly dispersed systems.

It must be emphasized that comparable results may be obtained only by use of one and the same kind of membrane. The precipitation membranes of copper ferrocyanide and tannic acid-protein, for example, are impermeable even to many *molecular* dispersoids and may, therefore, give rise to the phenomena of osmotic pressure (see the following paragraphs).

2. Methods of Dialysis.—Parchment tubes, parchment diffusion thimbles, reed tubes, fish bladders, urinary bladders, egg membranes and amniotic membranes are most used in the dialysis of colloids.[1] Membranes of collodion, as first used in colloid studies by G. Malfitano,[2] are especially convenient in many respects. Their preparation is discussed in the practical introducion (p. 10). Several forms of dialyzers were illustrated on page 11.[3] Because of their historical interest, Figs. 50, 51 and 52 are introduced, which are copies of the two types of apparatus which Graham used in the great work upon which colloid chemistry is built.

In dialyzing non-aqueous liquids, the effect of the dispersion medium upon the membrane must be considered. A possible chemical effect of the substances subjected to dialysis must also be kept in mind, though such is rarely met with among the colloids.

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[1] A detailed discussion of dialysis and its methods may be found in R. P. von Calcar, Dialyse, Eiweisschemie und Immunität, Leipzig-Leiden, 1908.

[2] G. Malfitano, Compt. rend., **139**, 1221 (1904).

[3] For a new form see R. Zsigmondy and R. Heyer, Z. f. anorg. Chem., **68**, 916 (1910).

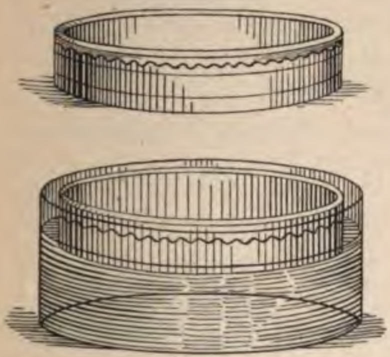

FIG. 50.—*Thomas Graham's* disc dialyzer.

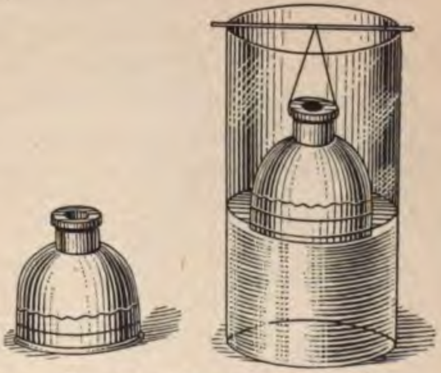

FIG. 51.—*Thomas Graham's* bell dialyzer.

3. Experimental Facts Regarding Dialysis of Colloids.—Since the days of Graham, almost every student of the general properties of colloid systems has made use of dialysis. It is, therefore, not possible to review all the work that has been done in this field. Generally speaking, dialysis teaches the same facts as diffusion.

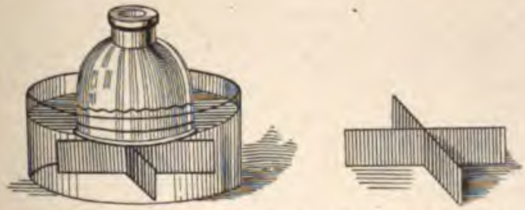

FIG. 52.—A second method of using *Graham's* bell dialyzer.

Thus, S. E. Linder and H. Picton (*l.c.*) were able to distinguish between dialyzing and non-dialyzing metallic sulphides. Of the many groups of compounds studied, only one will be discussed here, that of the technically and theoretically important water soluble dyes. F. Krafft and G. Preuner,[1] O. Teague and B. H. Buxton,[2]

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[1] F. Krafft and G. Preuner, Ber. d. Dtsch. chem. Ges., **32**, 1620 (1899).

[2] O. Teague and B. H. Buxton, Z. f. physik. Chem., **60**, 469 (1907).

H. Freundlich and W. Neumann,[1] R. Höber,[2] L. Vignon,[3] W. Biltz and F. Pfenning,[4] have all studied these. In Table 43 are reproduced some of the findings tabulated by Biltz. In connection with this table it should be noted that Krafft and Preuner used parchment tubes; Teague, Buxton, Höber and Vignon, parchment-paper thimbles, manufactured by Schleicher and Schüll; Biltz and Pfenning, collodion membranes. The solutions used were usually 0.1 percent; Teague and Buxton used 0.02 percent; Biltz and Pfenning 0.5 percent. The abbreviations in parentheses after the names of the dyes mark their origin.

TABLE 43.—DIALYSIS OF DYES

Typical Molecular Dispersoids

Name	Atomic number	Molecular weight	Dialyzes	Observer
Picric acid	19	229.0	Quickly.	Vignon.
Toluidin blue (Hoechst)	19	143.5	Quickly.	Biltz.
Naphthol yellow 9 (Bayer, Hoechst)	27	355.0	Quickly.	Höber, Vignon, Biltz.
Chrysoidin	30	214.0	Quickly.	Teague and Buxton.
Methylene blue	37	317.5	Quickly.	Krafft and Preuner, Teague and Buxton, Biltz.
Eosin	37	692.0	Quickly.	Teague and Buxton, Vignon, Biltz.
Erythrosin	37	880.0	Quickly.	Höber, Biltz.
Bengal rose	37	1050.0	Quickly.	Höber.
Quinolin yellow (Akt.)	40	477.0	Quickly.	Biltz.
True acid fuchsin B (Bayer)	41	467.0	Quickly.	Biltz.
Auramin O (Akt.)	43	303.5	Quickly.	Biltz.
Safranin	44	350.5	Quickly.	Teague and Buxton, Vignon, Biltz.
Wool violet S (Bad.)	46	445.0	Quickly.	Höber.
Brilliant crocein 3 B	51	556.0	Quickly.	Höber.
Acid fuchsin S (Akt.)	52	572.0	Quickly.	Vignon.
Methyl violet	56 to 66	393.5 to 469.5	Quickly.	Biltz.
Patent blue V (Hoechst)	84	804.0	Quickly.	Höber, Biltz.
Guinea green B	86	730.0	Quickly.	Höber.
Erioglaucin	95	782.0	Quickly.	Höber.

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[1] H. Freundlich and W. Neumann, Koll.-Zeitschr., **3**, 80 (1908).

[2] R. Höber, Koll.-Zeitschr., **3**, 76 (1908); Bioch. Zeitschr., **20**, 80 (1909).

[3] L. Vignon, Compt. rend., **150**, 619 (1910).

[4] W. Biltz (with F. Pfenning), van Bemmelen-Gedenkboek, 108, 1910.

Transition Systems between Molecular Dispersoids and Colloid Solutions

Name	Atomic number	Molecular weight	Dialyzes	Observer
Neutral red	37	288.5	Slowly	Teague and Buxton.
True red A (Akt. Bayer)	41	400.0	Slowly	Höber, Biltz.
Ponceau 2 R (Akt.)	45	480.0	Rather quickly	Höber, Biltz.
Ponceau B O extra (Akt.)	51	556.0	Rather quickly	Biltz.
Victoria black B (Bayer)	58	622.0	Only in traces	Biltz.
Nile blue	58	443.4	Slowly	Teague and Buxton.
Crystal violet	59	407.5	Rather quickly	Freundlich and Neumann, Vignon.
Aniline blue	74	565.5	Very slowly	Teague and Buxton. Höber.
Benzo-blue 3 B (Bayer)	86	960.0	Slowly	Höber.
Acid violet 6 B (Akt.)	91	733.0	Somewhat	Höber, Biltz.

Typical Colloid Solutions

Name	Atomic number	Molecular weight	Dialyzes	Observer
Cloth red 6 A (Akt.)	53	482.0	Not at all	Biltz.
Congo brown 9 (Akt.)	68	682.0	Not at all	Höber, Biltz, Teague and Buxton.
Congo red (Akt.)	70	606.0	Not at all	Vignon, Biltz.
Azo-blue (Akt.)	74	726.0	Not at all	Krafft and Preuner, Teague and Buxton, Höber, Biltz.
Benzopurpurin	76	724.0	Not at all	Krafft and Preuner, Höber, Biltz.
Congo blue B × 2B (Akt.)	80	860.0	Not at all	Biltz.
Night-blue	84	575.5	Not at all	Teague and Buxton, Freundlich and Neumann, Biltz.
Heliotrope B B (Bayer)	88	810.0	Not at all	Höber.
Chicago blue 6 B R W (Akt.)	88	992.0	Not at all	Biltz.

The table shows that, in general, dialyzability decreases with rising atomic number and increasing molecular weight. That the rule is only approximately true can be seen by comparing the tables horizontally. (The vertical rows are arranged according to increasing atomic numbers.) In each of the three classes, some of the dyes have a low, while some have a high, atomic number. Even substances with high molecular weights, as Bengal Rose may be found in the rapidly dialyzing class. The degree of dispersion of the dye is therefore dependent *not* alone on the atomic number or the molecular weight, but on other factors as well. It seems natural to try to explain the lack of parallelism through the chemical constitution of the dyes, as W. Biltz and others have done with a fair degree of success. A review of Biltz's results is beyond the limits of this book, but it should be noted that even so, a quantitative relation between chemical constitution and degree of dispersion does not appear even when only simple compounds in homologous series are considered. The absence of parallelism between size of particles and molecular weight demonstrates also the danger of trying to determine molecular weight from diffusion constants as discussed on p. 223.

When the dialysis of non-aqueous colloids is discussed it must first be remembered that many dyes "dissolve" to form colloid solutions in water, but molecularly dispersed ones in other solvents, such as alcohol (F. Krafft, *l.c.*, and others). Corresponding herewith, the alcoholic solutions dialyze better than the aqueous ones. Especially interesting results have been obtained with iodine dissolved in different organic solvents. J. Amann[1] has shown that iodine dissolves in benzene as a molecular dispersoid, in petroleum as a colloid. Corresponding to this fact, it dialyzes through a parchment thimble out of its solution in benzene but not out of that in petroleum.[2]

4. Special Observations Regarding the Dialysis of Colloids.—Colloids frequently pass through a dialyzing membrane *for a short time immediately following their preparation.* This is especially true of freshly prepared silicic acid as observed by Th. Graham and more recently confirmed by F. Mylius and E. Groschuff.[3] The explanation of this interesting fact is to be found in the *instability* of the degree of dispersion in colloid systems. When a colloid solution is prepared by condensation of a molecularly dispersed system, the desired product is not obtained at once, but only after hours or days. Sometimes, moreover, the condensation occurs

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[1] J. Amann, Koll.-Zeitschr., **7**, 235 (1910); **7**, 67 (1910).

[2] According to the unpublished results of Prof. S. Suzuki and the author.

[3] F. Mylius and E. Groschuff, Ber. d. Dtsch. chem. Ges., **39**, 119 (1906).

unequally, in other words, a few colloid particles are first produced but their number gradually increases with time, at the expense of the molecularly dispersed. It is to such changes that the behavior of silicic acid, of many albumin solutions, of humic acid, etc., must be referred.

Another phenomenon of both practical and theoretical importance is the *chemical decomposition through dialysis of molecularly dispersed substances with formation of a colloid phase.* It was known to Graham and belongs to the earliest methods of preparing colloid systems. It is essential that the original material suffer hydrolysis in water, yielding an insoluble, or but slightly soluble, component. This is true of the chlorides, nitrates, acetates, etc., of the metals. Since the molecularly soluble product of the hydrolysis passes through the dialyzing membrane while the "insoluble" component remains behind in colloid form, a continual displacement of the hydrolysis takes place, favoring the formation of the colloid. To obtain the corresponding colloid hydrate it is only necessary, therefore, to place the proper salt solutions in the dialyzer.

From the abundant literature describing these phenomena we may cite the following example of the chemical changes exhibited by iron hydroxide-iron chloride solutions, during dialysis, as observed by S. E. Linder and H. Picton.[1] Table 44 shows the changes in composition of the outer liquid during the process.

TABLE 44.—CHANGE IN COMPOSITION OF OUTER LIQUID DURING DIALYSIS OF IRON HYDROXIDE-IRON CHLORIDE SOLUTIONS

(According to S. E. Linder and H. Picton)

Time of dialysis in hours	Relation of Fe to HCl in outer liquid
0	56:109.5
24	56:137.0
48	56:609.0
120	56:1086.0
168	Not demonstrable: evident

Toward the end of the experiment, as can be seen, only HCl passed through the dialyzing membrane.

The changes in composition of the inner liquid during the dialysis is shown in Table 45.

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[1] S. E. Linder and H. Picton, Trans. Chem. Soc., Lond., 1909 (1905).

TABLE 45.—CHANGES IN COMPOSITION OF INNER LIQUID DURING DIALYSIS OF IRON HYDROXIDE-IRON CHLORIDE SOLUTIONS

(According to S. E. Linder and H. Picton)

Time of dialysis in days	Composition in grams per 100 cc.			Calculated molecular weight
	Fe	Cl	Formula	
5	1.2303	0.1410	13 $Fe(OH)_3$, $FeCl_3$	1767
9	1.2300	0.1110	20 $Fe(OH)_3$, $FeCl_3$	2302
10	1.7200	0.1250	25 $Fe(OH)_3$, $FeCl_3$	2837
17	1.5000	0.0773	36 $Fe(OH)_3$, $FeCl_3$	4014
30	1.2400	0.0550	42 $Fe(CH)_3$, $FeCl_3$	4656
37	1.1800	0.0490	45 $Fe(OH)_3$, $FeCl_3$	4977
44	1.1400	0.0460	46 $Fe(OH)_3$, $FeCl_3$	5084
61	1.0400	0.0430	45 $Fe(OH)_3$, $FeCl_3$	4977
210	0.6550	0.0150	82 $Fe(OH)_3$, $FeCl_3$	8936
Gels separated out after 120 days.	per gram Fe	0.012Cl	162 $Fe(OH)_3$, $FeCl_3$	17496

The table shows plainly the relative increase in iron hydroxide content at the cost of the hydrochloric acid. The formulas of the iron compounds produced and their respective molecular weights, as calculated by Linder and Picton, are also given. The impossibility of isolating the compounds, coupled with the fact that they show a progressive change makes the chemical significance of the numbers assigned as molecular weights rather fanciful. On the other hand, they demonstrate very well the progressive transformation into the colloid.

The progressive decomposition during dialysis, with formation of colloid in such solutions can be shown in a striking manner, according to N. Sahlbom,[1] by "capillarizing" them, that is, by dipping strips of filter paper into them. If this is done every 24 hours to ferric chloride or ferric nitrate undergoing dialysis, pictures are obtained like those shown in Figs. 53 and 54. At the beginning of dialysis the molecularly dispersed solution ascends the paper without decomposition and concentrates high up, as shown by the dark bands at the tops of the colored columns. After 1 or 2 days, the upper concentrated salt zone begins to disappear while a second less-colored one appears below. The latter consists of colloid iron hydroxide which when first formed is highly dispersed.

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[1] N. Sahlbom, Kolloidchem. Beihefte, 2, 79 (1910).

With progressing dialysis, the molecularly dispersed salt disappears entirely at the expense of the iron hydroxide, which gradually acquires the properties of a typical, positively charged colloid and therefore ascends filter paper little, if at all, as described on p. 15.

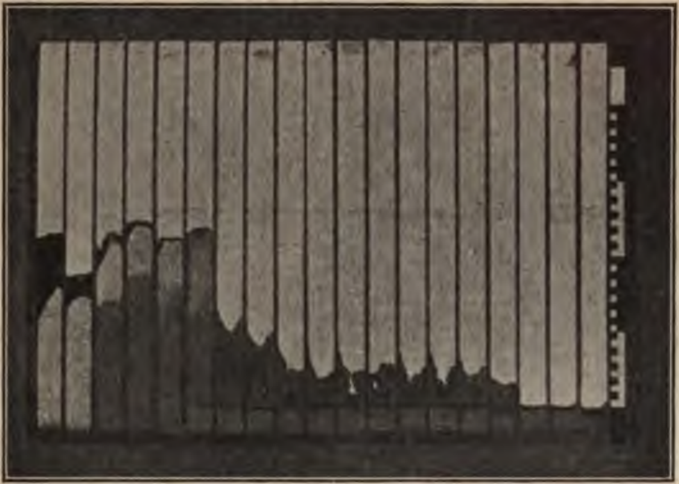

FIG. 53.—Dialysis of a ferric chloride solution. (Accordimg to *N. Sahlbom.*)

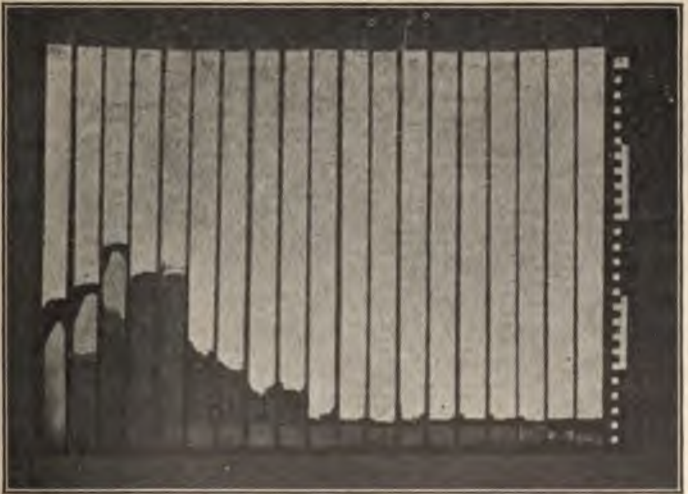

FIG. 54.—Dialysis of a ferric nitrate solution. (According to *N. Sahlbom.*)

Finally, a third phenomenon often observed during dialysis

TABLE 45.—CHANGES I
OF IRON H
(Accordin

Time of dialysis in days
5
9
10
17
30
37
44
61
210
Gels separated out after 120 days.

The table sh
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ment of a uniform spatial
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the dispersed phase cannot
outer[1] outer dispersion medium,
dispersion medium wanders into
this which represents the re-
alization, as far as possible, of
substances in the different parts

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[1] N. Sa

knowledge of osmosis see Wilh. Ostwald,
1903.

The intensity of the tendency to bring about a uniform distribution of dispersed phase and dispersion medium may be measured by opposing this osmotic leveling process by the hydrostatic pressure of a water column. The pressure thus made evident is called the *osmotic pressure* of the dispersoid.[1] To make osmosis possible it is immaterial whether the selective permeability of the membrane is brought about by its sieve-like action, which holds back mechanically the dispersed phase, or by its selective properties as a solvent in the sense that only the dispersion medium is soluble in it.[2]

Osmotic pressure and osmotic phenomena like Brownian movement and diffusion velocity are markedly dependent on the specific surface of the dispersed phase. Colloid solutions, therefore, show but slight osmotic pressures, provided they are not contaminated with molecular or ionic dispersoids. Most colloids can only with difficulty be rid of such impurities which enter these systems in the process of their preparation or are necessary for their stability. Such traces of impurities introduce great errors into pressure measurements which at the best yield but small values.[3] It cannot, however, be denied that many typical colloids, especially when of high dispersion, possess some osmotic pressure of their own. This follows as a necessary conclusion from the existence in them of Brownian movement and diffusibility.

Measurements of the osmotic pressure of colloids have been made and discussed at special length by W. Pfeffer,[4] H. Picton and S. E. Linder,[5] C. E. Linebarger,[6] E. H. Starling,[7] C. J. Martin,[8]

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[1] In many textbooks, following the lead of W. Nernst, we find it stated that osmotic pressure is the "cause" or "force" producing diffusion. This way of putting it is incorrect as the above remarks on the relation of diffusion to osmosis show and as J. J. van Laar (Vorträge über d. thermodynam. Potential usw. Braunschweig, 1906) has long emphasized. The concept of osmotic pressure stands and falls with the presence and absence of a selectively permeable membrane. It contradicts every correct view of osmotic pressure to assume its existence in the absence of such a membrane, as in the processes of free diffusion. It is, however, correct to hold that the phenomena of diffusion, of osmosis and of Brownian movement all spring from the same source of energy as clearly evidenced by the close relations and analogies between them.

[2] For details regarding such and other properties of membranes see the comprehensive monograph of H. Zangger, Ergebnisse der Physiologie, **7**, 99 (1908).

[3] With reference to the view that admixed electrolytes may constitute integral parts of the colloids see p. 143.

[4] W. Pfeffer, Osmotische Untersuchungen, Leipzig, 1877.

[5] H. Picton and S. E. Linder, Journ. Chem. Soc., **63**, 148 (1892).

[6] C. E. Linebarger, Silliman's Am. Journ. Sci. (3), **43**, 218, 416 (1892).

[7] E. H. Starling, Journ. Physiol., **19**, 312 (1895–6); **24**, 317 (1899).

[8] C. J. Martin, Journ. Physiol., **20**, 364 (1896).

A. Lottermoser,[1] B. Moore, W. H. Parker, H. E. Roaf, L. Adamson, D. Bigland,[2] E. W. Reid,[3] J. Duclaux,[4] G. Malfitano,[5] R. S. Lillie,[6] G. Hüfner, Gansser,[7] W. M. Bayliss,[8] W. Biltz and A. von Vegesack[9] and others. Only the more important of their findings can be touched upon here.

2. Methods of Measuring the Osmotic Pressure of Colloids.—From what has been said it is clear that any dialyzing apparatus may be used to measure osmotic pressure. As dialyzing membranes, the earlier investigators generally used parchment paper. More recently collodion thimbles have been employed. C. J. Martin (*l.c.*) used clay cups impregnated with silicic acid gels; E. H. Starling (*l.c.*), the same impregnated with gelatine. For details the recent papers of W. Biltz and A. von Vegesack should be consulted. Fig. 55, which represents a cell used for osmotic pressure measurements, is taken fron their publications. Below is shown the collodion thimble. Of the two vertical tubes, one is used to fill the "osmometer," the other to record the pressure.

The greatest source of error in the determination of the osmotic pressure of colloids lies in the disturbing effects of the presence of molecularly dispersed phases, especially electrolytes. Several schemes have been proposed to obviate the difficulty. Different investigators, especially B. Moore (with his collaborators) and J. Duclaux, have maintained that the accompanying electrolytes constitute integral parts of the colloid and are bound to it either chemically (see Duclaux) or at least through "adsorption." In other words, they hold the electrolytes to be essential to the maintenance of the colloid state. When they are removed the colloid is "denatured" and, as has been observed, "polymerized" into coarsely dispersed particles, even to the point of coagulation. That all this may occur, as in the case of the albumins, must be admitted, but it cannot be stated as a universal truth. As R. S. Lillie (*l.c.*) has emphasized, the presence of electrolytes is not essential to the existence of all metallic hydrosols, and no reason can be assigned at present why one phase cannot be dispersed into another to the point of colloid dispersion in the entire absence of any electrolyte. These remarks are not intended to deny the existence of colloid-electrolyte complexes. They are only made to emphasize that such discussion does not answer the question of what is the value of the osmotic pressure of pure colloids themselves and how it may be measured, for theoretically the colloids must have some, for they show Brownian movement and diffuse.

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[1] A. Lottermoser, Anorg. Kolloide, Stuttgart, 1901; Z. f. physik. Chem., **60**, 451 (1907).

[2] B. Moore and W. H. Parker, Amer. Journ. Physiol., **7**, 261 (1902); B. Moore and H. E. Roaf, Bioch. Journ., **2**, 34 (1906); **3**, 55 (1907); B. Moore and D. Bigland, *ibid.*, **5**, 32 (1909); H. E. Roaf and L. Adamson, Bioch. Journ., **3**, 422 (1908); Journ. Physiol., **39** (1909); Quart. Journ. Physiol., **3**, 75, 171 (1910); in part available only in abstract.

[3] E. W. Reid, Journ. Physiol., **31**, 439 (1904); **33**, 12 (1905).

[4] J. Duclaux, Compt. rend. **140**, 1468, 1544 (1905); Journ. Chim. physique, **5**, 40 (1907); **1**, 407 (1909); see also the review in Koll.-Zeitschr., **3**, 126 (1908).

[5] G. Malfitano, Compt. rend., **142**, 1418 (1906).

[6] R. S. Lillie, Amer. Journ. Physiol., **20**, 127 (1907).

[7] G. Hüfner and Gansser, Engelmann's Arch. f. Physiol., 209 (1907).

[8] W. M. Bayliss, Proc. Roy. Soc., **81**, 269 (1909); Koll.-Zeitschr., **6**, 23 (191).

[9] W. Biltz and A. von Vegesack, Z. f. physik. Chem., **68**, 357 (1909); **73**, 481 (1910).

The following measures have been proposed to attain this end. At first sight it would seem most satisfactory to use membranes which permit a sharp dialytic separation of colloids and molecular dispersoids. In the course of the dialysis the molecular dispersoids would then pass through the membrane while the colloids would remain behind. The end pressure would then be that of the pure colloid. It is well to emphasize, at once, that these final osmotic pressures have almost invariably been found to be *very low*.

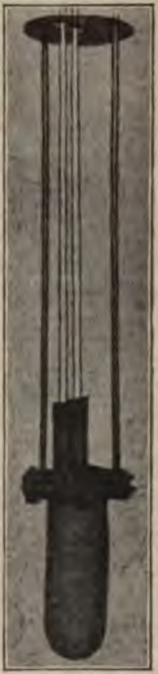

FIG. 55.—Osmometer of *W. Biltz* and *A. von Vegesack.*

A second method consists in taking a limited volume of outer liquid and waiting until an equilibrium has been established between the concentration of the electrolytes in this and the concentration of those contained in the inner liquid. In connection with this method it must be borne in mind that the equilibrium need not in any sense be synonymous with equality of concentration in the two liquids. A whole series of facts, one of which is the difficulty of "washing out" the last traces of electrolytes from precipitates, compels the conclusion that *colloids tend to concentrate electrolytes upon themselves* and thereby to increase the possibility of developing and exhibiting a greater osmotic

It is a remarkable fact that while the osmotic pressure of gelatine is increased by shaking, that of egg-albumin is decreased.

Table 48 illustrates the influence of stirring on the osmotic pressure of colloid solutions.

TABLE 48.—INFLUENCE OF STIRRING ON OSMOTIC PRESSURE OF BENZOPURPURIN SOLUTIONS.

(According to W. Biltz and A. von Vegesack)

A. Benzopurpurin low in electrolytes			B. Benzopurpurin high in electrolytes		
Hours	Height of fluid column	Remarks	Hours	Height of fluid column	Remarks
1.0	9.41	Not stirred	5	1.22	Stirred.
2.5	9.62	Not stirred	15	1.25	Not stirred.
3.5	9.50	Not stirred	18	1.34	Stirred.
4.5	9.68	Stirred 5 min	378	1.30	Stirred 1 hr. daily.
5.0	9.86	Stirred 5 min	426	1.24	Stirred 7 hrs. previously.
5.5	10.07	Stirred 5 min			
6.0	10.18	Stirred 5 min	450	1.26	Stirred 7 hrs. previously.
7.0	10.40	Stirred 5 min			
8.0	10.60	Stirred 5 min			
9.0	10.64	Stirred 5 min			
10.0	10.66	Stirred 5 min			
20.0	8.16	Not stirred			
20.5	8.37	Stirred 5 min			
21.0	8.92	Stirred 5 min	0	.....	....
21.5	9.08	Stirred 5 min	100	1.14	Stirred during day.
22.0	9.16	Stirred 5 min	121	1.19	Stirred 6 hrs.
23.0	9.29	Stirred 5 min	145	1.09	Stirred 6 hrs.
24.0	8.98	Stirred 5 min	167	1.10	Stirred 6 hrs.
25.0	8.99	Stirred 5 min			
28.0	7.16	Not stirred.			
28.5	7.45	Stirred 5 min			

This table shows an increase in osmotic pressure with every stirring, even though the effect is but transitory. The increase occurred three times in the data given. It is also apparent that solutions containing small amounts of electrolytes are more sensitive to this influence than those richer in these which are scarcely affected. Gelatine behaves similarly, as shown in Table 47.

In discussing the influence of *time* upon the osmotic pressure of colloids we need to distinguish between its variations when a colloid is simply left to itself in an osmometer and its variations if the same colloid is measured at different periods. The first relation is evidenced in the left-hand column of Table 48. This benzopurpurin showed a rise to 1.21 cm. after 310 hours; while the *capillary* rise in a similar tube amounted to 1.12 cm. The osmotic pressure was therefore 0.09 cm. In illustration of the influence of *age* upon the solutions, these authors found a dialyzed solution of 0.00103 normal night-blue to yield a maximum osmotic pressure of 15.52 cm. of water after 2 days; after 6 days, 4.24 cm.; and after 11 days, 4.08 cm.

When we survey these facts we are struck by the great inconstancy of the osmotic pressure of colloids as compared with that of molecularly dispersed solutions. The osmotic pressure of colloids is variable, being greatly modified by mechanical treatment, age, etc. Such sensitiveness is unknown in molecular dispersoids. It is true, of course, that the experiments of W. Spring[1] have shown that even ordinary salt solutions, for example, are not absolutely stable in their conductivity, their optical properties, etc., but these variations are very small when compared with those exhibited by colloids. The reasons for this great variability are to be sought in the *changes of state* of colloids, such as variations in their degrees of dispersion, states of aggregation, etc., for which many different causes may be responsible, as will be discussed later. The osmotic pressure of colloids, more especially of emulsoids, varies therefore as does their viscosity.

4. Influence of Concentration on Osmotic Pressure of Colloids.—The osmotic pressure of molecular dispersoids, as is well known, is governed by the important law of Pfeffer-van't Hoff: the *osmotic pressure is directly proportional to the concentration.* The relations in colloid systems are not so simple. Examples are known, in which the law holds approximately, but there are also those in which the osmotic pressure *increases faster than the concentration, or more slowly than this.* Perhaps nothing better demonstrates the inappropriateness of applying without due consideration, the "solution laws" valid for molecularly dispersed systems to colloid systems, than this variability of the concentration function of the osmotic pressure of colloids.

The following results of W. Biltz and A. von Vegesack (*l.c.*) on purified congo red may serve to illustrate the first of the three possibilities, namely, that wherein concentration and osmotic pressure are approximately proportional. W. M. Bayliss (*l.c.*) also noted this proportionality in concentrations ranging from 0.07 to 1 percent by weight.

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[1] W. Spring, Koll.-Zeitschr., **7**, 22 (1910), where references to earlier papers on this subject may be found.

TABLE 49.—RELATION OF OSMOTIC PRESSURE TO CONCENTRATION IN DIALYZED CONGO RED SOLUTIONS

(According to W. Biltz and A. von Vegesack)

Concentration C	Osmotic pressure in cm. p	$\frac{p}{C}$ = const.
0.539 norm.	4.15 cm.	0.770
1.08	8.15 cm.	0.755
1.44	10.24 cm.	0.695
1.80	14.00 cm.	0.778
2.155	14.62 cm.	0.678
2.87	18.70 cm.	0.652
3.23	21.55 cm.	0.667
3.59	25.04 cm.	0.698
4.31	25.30 cm.	0.587

The constants are all of about the same order of magnitude. Gum arabic behaves similarly according to W. Pfeffer (*l.c.*).

TABLE 50.—OSMOTIC PRESSURE OF GUM ARABIC IN DIFFERENT CONCENTRATIONS

(According to W. Pfeffer)

Concentration C	Osmotic pressure in cm., Hg. p	$\frac{p}{C}$
1 percent	6.59	6.9
6	25.9	4.3
14	70.0	5.0
8	119.0	6.6

The observations of J. Duclaux (*l.c.*) on the same substance and given in Table 51 should be compared with these.

Some illustrations of how the osmotic pressure may increase more rapidly than the concentration are given in Table 51.

As readily apparent, the ratio $\frac{p}{C}$ increases greatly with rising concentration. This is altogether different from the behavior of molecular dispersoids, in which, so far as known, the opposite occurs as the concentration rises. That the experimental methods

TABLE [illegible]. RELATION OF OSMOTIC PRESSURE OF DIFFERENT COLLOIDS TO THEIR CONCENTRATION
(According to J. Duclaux)

Iron hydroxide sol			Colloidal copper ferrocyanide			Thorium hydroxide sol			Gum arabic			Caramel		
c	p	p/c	c	p	p/c	c	p	p/c	c	p	p/c	c	p	p/c
Percent	Cm.		Percent	Cm.		Percent	Cm.		Percent	Cm.		Percent	Cm.	
about [illegible]	[illegible]	about [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	10	[illegible]	1.6	5.1	[illegible]
about [illegible]	[illegible]	about [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	75	[illegible]	4.3	10.0	[illegible]
about [illegible]	[illegible]	about [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	444	[illegible]			
about [illegible]	[illegible]	about [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]						
about [illegible]	[illegible]	about [illegible]				[illegible]	[illegible]	[illegible]						
						[illegible]	[illegible]	[illegible]						
about [illegible]	[illegible]	[illegible]												
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about [illegible]	[illegible]	[illegible]												

According to W. Biltz and A. von Vegesack (l.c.) the osmotic pressure of a 0.105 percent iron hydroxide sol amounts to 3.74 cm. after 4 hours; that of a 0.175 percent one to only 1.49 cm. after 5 hours.

possibilities, namely, that wherein concen pressure are approximately proportional. also noted this proportionality in conc 0.07 to 1 percent by weight.

TABLE 49.—RELATION OF OSMOTIC PRESSURE
CONGO RED SOL
(According to W. Biltz and

Concentration C	Osmotic press p
0.539 norm.	4.1
1.08	8
1.44	10
1.80	1
2.155	1
2.87	
3.23	
3.59	
4.31	

s in easin cular rker (l tion sho while a The tw her words, and one-h taining the e W. Reid (*l.c.*) hemoglobin, illu

The constants are al Gum arabic behaves si

TABLE 50.—OSMOTIC PRE

Concentration C
1 percent
6
14
8

HEMOGLOBIN SOLU

Reid

pressure mm. Hg.	Osmotic per 1 pe Hemo $=\frac{p}{C}$
12 mm.	4.
12	4.1
17	3.
10	3.8
17	3.
22	3.
23	3.

The obse and given i Some il more rapi

As r conce of m occ

slight irregularities, the decrease noticeable. The differences are brought ou the variation of the quotient, $\frac{p}{C}$, is represented This has been done (in arbitrary units) in Fig. 53 types are easily recognized.

be mentioned that J. Duclaux (*l.c.*, 1910) minimum for the quotient in the case of Berli though he has himself raised some doubts as to the reliability of his measurements.[1]

The theoretical significance of these different concentration curves we shall discuss later (see p. 262).

5. Influence of Temperature on Osmotic Pressure of Colloids.—C. J. Martin and W. M. Bayliss (*l.c.*) state that the osmotic pressure of albumin, hemoglobin and congo red varies rectilinearly with the temperature, in other words, directly with the absolute temperature. This statement would make Gay-Lussac's law valid for these solutions. The findings of B. Moore and Roaf (*l.c.*), J. Duclaux (*l.c.*), W. Biltz and A. von Vegesack (*l.c.*),

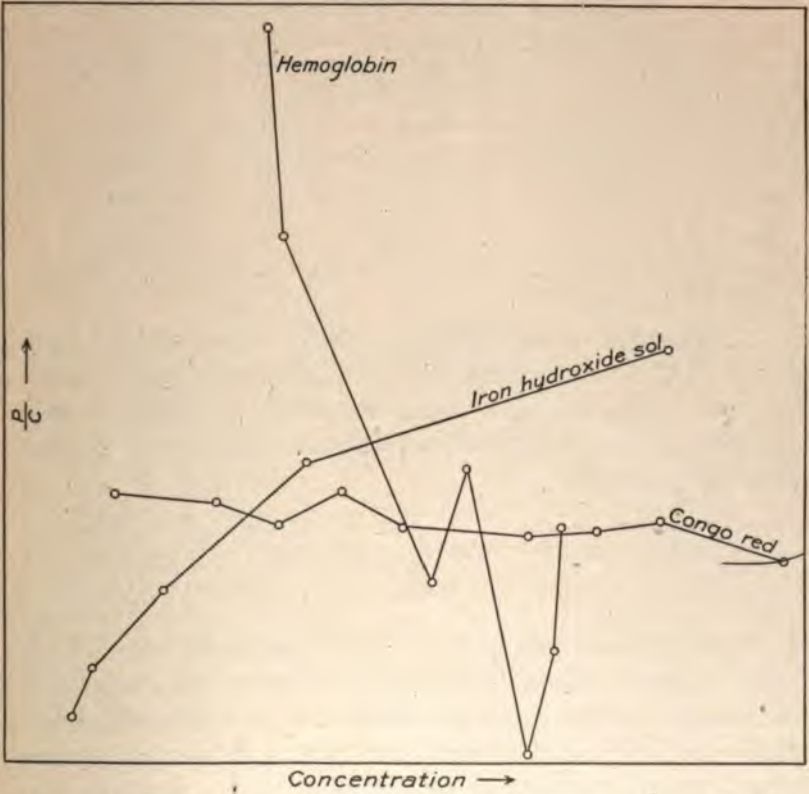

FIG. 56.—Relation between concentration in colloid systems and the quotient of the osmotic pressure and concentration.

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[1] The measurements of W. Pfeffer on gum arabic, given in Table 50, also show a minimum value for the quotient $\frac{p}{C}$.

contradict this. Moore and Roaf found the osmotic pressure of gelatine solutions to increase considerably faster than the absolute temperature. Technical night-blue solutions show an analogous behavior, according to the figures of W. Biltz and A. von Vegesack, contained in Table 53.

TABLE 53.—INFLUENCE OF TEMPERATURE ON OSMOTIC PRESSURE OF A 3.49 NORMAL SOLUTION OF TECHNICAL NIGHT-BLUE
(According to W. Biltz and A. von Vegesack)

Temperature $t°$	$T°$	Osmotic pressure in cm. p	$\frac{p}{T}$
0	273	6.21	0.022
25	298	10.81*	0.036
50	323	13.83	0.043
70	343	17.69	0.050

*Average of two experiments.

J. Duclaux has observed the opposite to be true of iron hydroxide sol. In this, the osmotic pressure decreases not only *relatively*, but even *absolutely*, with rising temperature. There exists no analogue for this in the field of molecular dispersions. Duclaux found the following:

Temperature..........	2° (275)	25° (298)	70° (343)
Osmotic pressure (cm.).	22.9	21.3	20.9
$\frac{p}{T}$....................	0.083	0.071	0.061

Figure 57 shows graphically how differently the osmotic pressure of different colloids varies with changes in the temperature. The dotted line represents the ideal case in which there exists simple proportionality between the two as is the case, at least approximately, in molecular dispersoids.

It should now be pointed out that B. Moore and Roaf (*l.c.*) and R. S. Lillie (*l.c.*) observed interesting *thermal after-effects* or so-called *hysteresis phenomena* in gelatine solutions. Thus gelatine solution which has been heated continues to show a higher osmotic pressure for some time after cooling than when kept continuously at the lower temperature. The following Table 54 taken from R. S. Lillie illustrates this. It also shows that the differences first noted between the previously cooled and the previously warmed gelatine become less with time.

OF THERMAL HISTORY ON OSMOTIC PRESSURE OF
1 PERCENT GELATINE
(According to R. S. Lillie)
otic Pressure at Room Temperature in Mm. Hg.

the solution	Previously chilled on ice	Previously warmed to 65–70°
1 day	5.0	6.4
5 days	5.0	5.3
2 days	4.9 (chilled for long time previously)	6.0
1 day	5.7	6.2
1 day	5.6	6.0

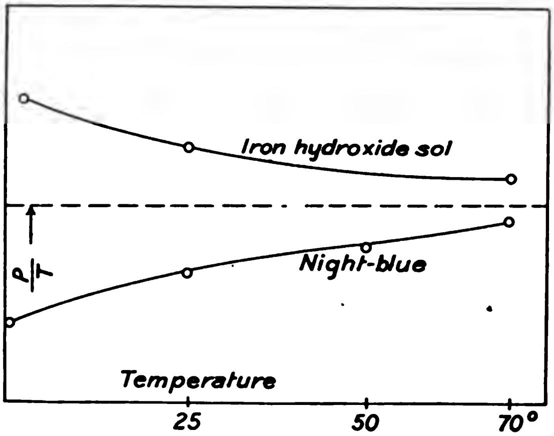

FIG. 57.—Relation between the temperature of colloids and the quotient of osmotic pressure and absolute temperature.

This behavior also is unknown among the molecular dispersoids.

6. Influence of Added Substances on Osmotic Pressure of Colloids.—The influence of added substances upon the osmotic pressure of a given system, is, according to the classic theory of molecularly dispersed solutions, purely additive. In other words, the pressure exerted by the added substance is added to that of the original system. There exist exceptions to this rule, of course, and usually in the sense that the calculated osmotic pressures are found to be greater than those actually observed.

The effect of added substances on the osmotic pressure of colloid systems is more complicated. Under this heading also, concentration and temperature functions are encountered which not only do not correspond with any observed among molecular dispersoids, but which among themselves show great differences.

The influence of added substances may be studied by adding them in equal concentration to both the inner and the outer liquid. The important experiments of R. S. Lillie (*l.c.*) were carried out in this way.

Acids and *alkalies* may either increase or decrease the osmotic pressure of different colloids. Sometimes one and the same colloid may show both types of behavior. Often very small quantities of hydrogen or hydroxyl ions are sufficient to cause noticeable effects. W. M. Bayliss (*l.c.*) found the osmotic pressure of very pure (and highly dispersed) congo red to fall from 207 mm. to 120 mm. when the outer water (conductivity water) surrounding his osmometer was replaced by the same water saturated with carbon dioxide. The stronger acids produce, of course, still more marked effects. The addition of alkali *increases* the osmotic pressure until a maximum is reached, beyond which it falls again. Table 55 gives a part of R. S. Lillie's results with gelatine.[1]

TABLE 55.—INFLUENCE OF ACIDS AND ALKALIES ON OSMOTIC PRESSURE OF 1.5 PERCENT GELATINE
(According to R. S. Lillie)

Influence of HCl		Influence of KOH	
Concentration	Osmotic pressure in mm. Hg.	Concentration	Osmotic pressure in mm. Hg.
0	8.2	0	7.9
n/3100 HCl	6.8	n/3100 KOH	14.1
n/2050	12.3	n/620	23.7
n/1550	17.9	n/412	25.1
n/1024	26.5	n/310	29.0
n/770	32.4		
n/620	34.9		
n/412	39.3		

As can be seen, low concentrations of acid lead to a slight but definite *minimum* of osmotic pressure. With higher concentrations there occurs a sharp *increase* in osmotic pressure which rises steadily for a time with increasing concentration. R. S. Lillie thinks it probable that beyond a certain point a decrease in osmotic pressure would again occur. Within the concentration range studied, alkalies led only to an *increase* in osmotic pressure.

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[1] See also the analogous findings of H. E. Roaf (*l.c.*) on hemoglobin.

Figure 58 shows graphically this variation of the osmotic

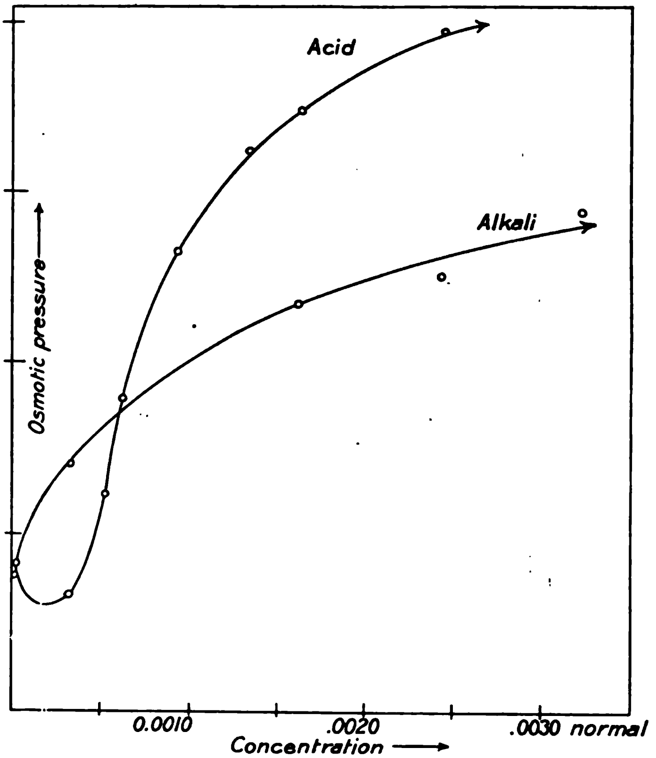

FIG. 58.—Effect of acid and alkali upon the osmotic pressure of a 1.5 percent gelatine solution. (According to experiments by *R. S. Lillie.*)

pressure of gelatine solutions with the concentration of the added acids and bases.

Contrary to the findings in the case of gelatine, the osmotic pressure of egg albumin is *always lessened* by the addition of hydrogen or hydroxyl ions. Table 56 shows this.

In the case of the acids a definite minimum again appears. The type of curve, at least for albumin, is therefore not so fundamentally different from that for acid gelatine.

TABLE 56.—INFLUENCE OF ACIDS AND ALKALIES ON OSMOTIC PRESSURE OF 1.5 PERCENT EGG ALBUMIN
(According to R. S. Lillie)

HCl		KOH	
Concentration	Osmotic pressure in mm. Hg.	Concentration	Osmotic pressure in mm. Hg.
0	25.6	0	25.6
n/3100 HCl	20.7	n/3100 KOH	24.1
n/1240	11.5	n/1240	22.6
n/620	14.1	n/620	20.2
n/412	20.4	n/412	18.0
n/310	22.2	n/310	17.9

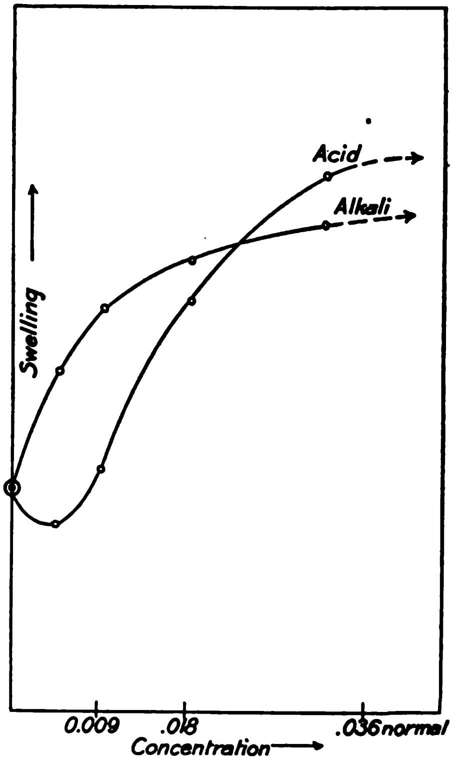

FIG. 59.—Effect of acid and alkali on the swelling of gelatine plates. (According to experiments by *Wo. Ostwald.*)

To illustrate the varied influence of salts the following examples may be given. Technical night-blue contains a considerable admixture of electrolytes. If they are removed by dialysis its osmotic pressure *increases*, as shown in Table 57.

W. M. Bayliss (*l.c.*) obtained analogus results for congo red.

The behavior of gelatine and albumin toward added salts has

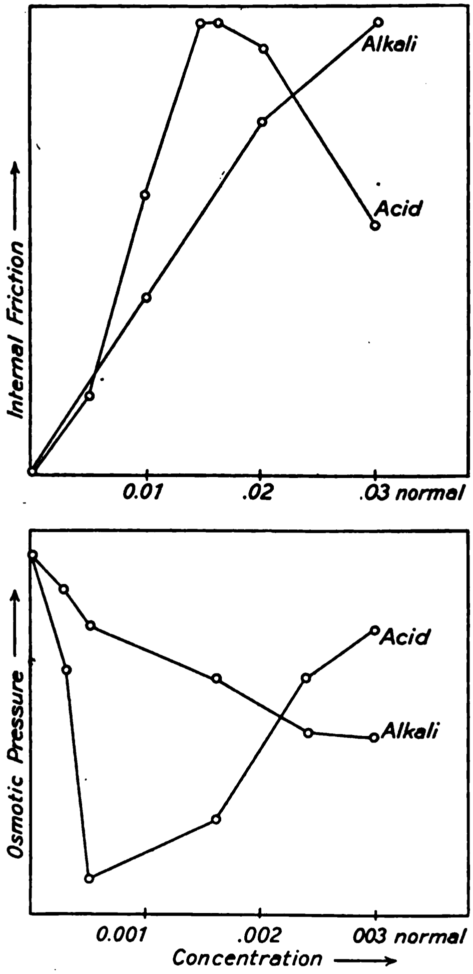

FIG. 60.—Relation between internal friction (upper figure) and osmotic pressure (lower figure) in albumin solutions when acid or alkali is added in different concentrations. (From experiments by *Wo. Pauli* and his co-workers and *R. S. Lillie.*) Only the percentage increase in viscosity and not its absolute value could be given in the upper figure.

been extensively studied (B. Moore and co-workers, R. S. Lillie, etc.). The following general truths are taken from the findings of R. S. Lillie:

TABLE 57.—OSMOTIC PRESSURE OF PURIFIED NIGHT-BLUE AND OF NIGHT-BLUE CONTAINING ELECTROLYTES

(According to W. Biltz and A. von Vegesack)

Purified colloid		Colloid containing electrolytes	
Concentration	Osmotic pressure in cm.	Concentration	Osmotic pressure in cm.
1.30	5.81	1.20	4.72
1.74	12.70	1.58	5.10
2.17	16.64	1.60	5.31
2.61	21.99	1.96	6.24
3.04	20.24	2.36	7.90
3.91	25.32	2.73	9.42
4.34	32.18	3.49	11.19
5.21	37.24	5.76	14.10
6.08	43.94	6.12	20.81

The addition of salts always causes a *decrease* in the osmotic pressure of these colloids. The degree of this decrease varies with the concentration and with the nature of the anion and cation. Generally speaking, the neutral salts of the alkali metals cause the smallest decrease. The salts of the alkaline earths are more effective and those of the heavy metals most effective of all, though they vary considerably among themselves. With salts having a common cation the order of the anions, when that most effective is given first, is about as follows:

$$SO_4 > Cl > NO_3 > Br > I > CNS$$[1]

The cations similarly arranged follow the order:

heavy metals > alkaline earths > alkali metals.

Table 58 details some of the actual experimental findings. If the validity of the above-mentioned conclusions is to be tested, the data of the original papers must be consulted for the experiments differ considerably among themselves.

Figures 61 and 62 also show the complicated effects of the *concentration* of the added salts upon the osmotic pressure. The original paper (*l.c.*, p. 111) must be consulted for the detailed data upon which these figures are based.

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[1] For similar findings on hemoglobin see the work on H. E. Roaf (*l.c.*).

TABLE 58.—INFLUENCE OF SALTS ON OSMOTIC PRESSURE OF COLLOIDS
(According to R. S. Lillie)

Salts of the alkalies				Salts of the alkaline earths			
1.25 percent albumin		1.25 percent gelatine		1.25 percent albumin		1.25 percent gelatine	
Concentration	Osmotic pressure in mm., Hg.	Concentration	Osmotic pressure in mm., Hg.	Concentration	Osmotic pressure in mm., Hg.	Concentration	Osmotic pressure in mm., Hg.
0	21.6	0	7.9	0	21.5	0	5.9
m/24 NaCl	5.0	m/24 KCl	3.3	m/96 $MgCl_2$	7.3	m/96 $MgCl_2$	3.2
m/24 NaBr	4.6	m/24 KBr	3.7	m/96 $CaCl_2$	7.6	m/96 $CaCl_2$	2.7
m/24 NaI	4.0	m/24 KI	3.7	m/96 $SrCl_2$	7.2	m/96 $SrCl_2$	3.1
m/24 $NaNO_3$	4.8	m/24 KNO_3	3.5	m/96 $BaCl_2$	7.6	m/96 $BaCl_2$	2.7
m/24 NaCNS	5.3	m/24 $KClO_3$	3.7				
m/24 Na_2SO_4	4.0	m/24 $KBrO_3$	3.6				
		m/24 KCNS	3.75				
		m/24 K_2SO_4	2.9				
		m/24 $KCOOCH_3$	3.4				
		m/24 $K_2C_2O_4$	3.4				

Salts of the heavy metals				Influence of different cations with common anion			
1.25 percent albumin		1.25 percent gelatine		1.25 percent albumin		1.25 percent albumin	
Concentration	Osmotic pressure in mm., Hg.	Concentration	Osmotic pressure in mm., Hg.	Concentration	Osmotic pressure in mm., Hg.	Concentration	Osmotic pressure in mm., Hg.
0	21.5	0	5.4	0	20.8	0	5.4
m/96 $MnCl_2$	6.9	m/192 $CoCl_2$	2.0	m/48 LiCl	5.4	m/48 LiCl	2.9
m/96 $CoCl_2$*	5.6	m/192 $CuCl_2$	3.3	m/48 NaCl	5.6	m/48 NaCl	2.6
m/96 $CdCl_2$*	4.1			m/48 KCL	5.9	m/48 KCl	2.4
m/96 $Pb(NO_3)_2$*	2.8			m/48 NH_4Cl	4.5	m/48 NH_4Cl	2.6
m/96 $CuCl_2$*	1.6						

* A precipitate is formed.

It is interesting to compare the behavior of the two colloids toward the *same* added substance. While the salts of the alkali metals produce about the same effect upon both (the sulphocyanate having the least effect, the sulphate the greatest) almost opposite effects are produced on albumin and gelatine when other salts are used. Among the alkaline earths, $SrCl_2$ and $MgCl_2$ produce a greater effect on albumin than $CaCl_2$ or $BaCl_2$. When gelatine is used the reverse is the case. Of the salts of the heavy metals, $CuCl_2$ affects albumin more than $CoCl_2$. The opposite is true for gelatine. Such contrary effects are not so evident when the cations are compared.

On the basis of the investigations of S. Posternak,[1] Wo. Pauli[2] and R. Höber,[3] we are, no doubt, correct in referring these differences in behavior to the differences in the reaction of the two colloids. Fresh (native) albumin, such as R. S. Lillie used, has a slightly *alkaline* reaction, while commercial gelatine is always *acid*. The differences in the effects of an added salt upon an "acid" or an "alkaline" albumin so far as its internal friction was concerned were discussed in §25. It is of much interest that the osmotic pressure of colloid systems should also be so greatly dependent on the acid or alkaline reaction of the colloid.

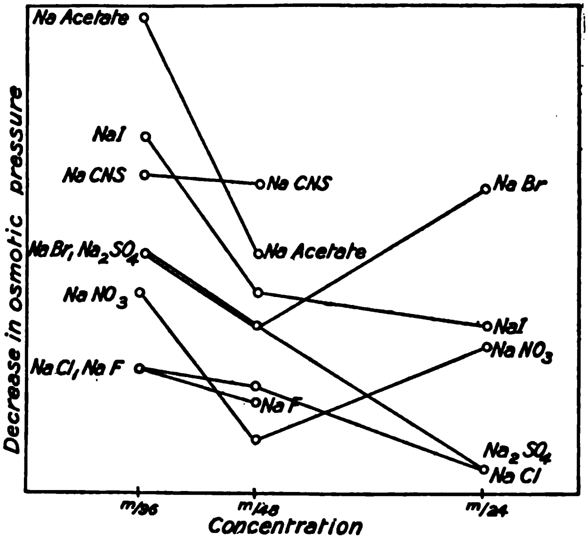

FIG. 61.—Effect of salts upon the osmotic pressure of gelatine. (According to *R. S. Lillie.*)

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[1] S. Posternak, Ann. de l'Inst.-Pasteur, 15, 85 (1909)
[2] Wo. Pauli, Hofmeister's Beitr., 5, 27 (1903).
[3] R. Höber, Hofmeister's Beitr., 11, 35 (1907).

The influence of electrolytes on the osmotic pressure of colloids may show hysteresis. The after-effects of temperature were discussed on p. 249. If, in the osmotic study of a gelatine + acid mixture, the outer liquid is replaced by distilled water, the pressure column gradually sinks. But to attain its original level requires days, and maybe weeks, before the osmotic pressure of the pure gelatine is again reached, even when the acid which dialyzes out very rapidly, is constantly removed by frequent changes of the water (R. S. Lillie). Such lagging before equilibrium is finally attained is unknown in the osmosis of molecular dispersoids.

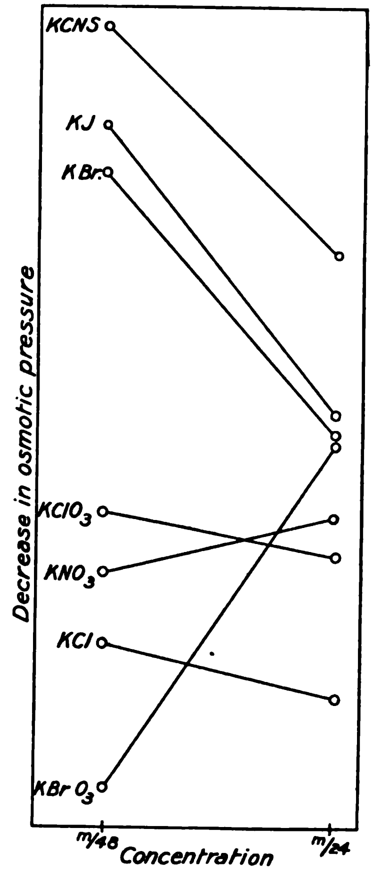

FIG. 62.—Effect of salts upon the osmotic pressure of albumin. (According to *R. S. Lillie.*)

Our knowledge of the influence of non-electrolytes on the osmotic pressure of colloids is still limited. An investigation of this question would doubtless bring out many interesting facts. Table 59 reproduces some of R. S. Lillie's (*l.c.*) results, in which but small differences of both a positive and a negative nature appear. Obviously, higher concentrations of alcohol, acetone, etc., might cause a decided decrease in the osmotic pressure of these colloids.

TABLE 59.—INFLUENCE OF NON-ELECTROLYTES ON OSMOTIC PRESSURE OF COLLOIDS
(According to R. S. Lillie)

Egg Albumin			
1.25 percent		1.6 percent	
Added substance	Osmotic pressure in mm., Hg.	Added substance	Osmotic pressure in mm., Hg.
0	22.4	0	29.4
m/6 cane sugar	21.5	m/6 glycerine	29.5
m/6 dextrose	21.8	m/6 urea	27.9
Gelatine 1.25 percent			
0	6.2	0	5.5
m/6 cane sugar	6.6	m/6 dextrose	5.7
m/6 dextrose	5.8	m/6 glycerine	5.6
m/6 glycerine	5.9	m/6 urea	6.6
m/6 urea	7.3		

7. On the Theory of Osmotic Pressure of Colloids.—In the classic theory of osmosis in molecularly dispersed systems, as formulated by J. H. van't Hoff, on the basis of W. Pfeffer's (*l.c.*) experiments, the absolute concentration, in other words, the *number of molecules in the unit volume* alone determines the amount of the osmotic pressure (at constant temperature). The osmotic pressure is directly proportional to the number of molecules and to the absolute temperature. Sv. Arrhenius assumed a dissociation of the molecules into ions, in the case of the electrolytes in which a gram molecule in the unit volume shows a higher osmotic pressure than that calculated. On the other hand, when unex-

The influence of electrolytes on the osmotic pressure of colloids may show hysteresis. The after-effects of temperature were discussed on p. 249. If, in the osmotic study of a gelatine + acid mixture, the outer liquid is replaced by distilled water, the pressure column gradually sinks. But to attain its original level

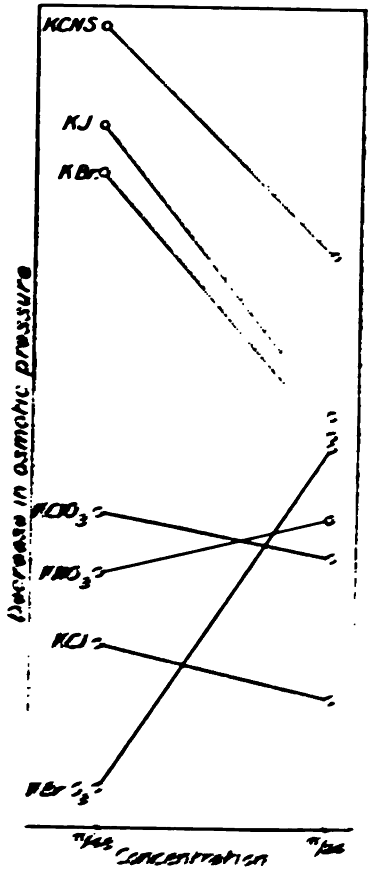

FIG. 62.—Effect of salts upon the osmotic pressure of albumin [illegible] according to [illegible]

requires days, and may be weeks, before the original pressure of the pure gelatine is again reached, even when the acid which dialyzes out very rapidly, is constantly removed by frequent changes of the water. [illegible] equilibrium is finally attained [illegible] dispersoids.

Only a theory of osmotic phenomena that considers the degree of dispersion of the system, in addition to concentration and temperature, can prove universally valid for all dispersed systems.

It is not difficult to bring experimental proof for such theoretical deductions. In fact, no one who tries to account for the great sensitiveness of the osmotic pressure of colloids to different influences, can escape considering changes in those characteristic variables of colloids, namely, their degree of dispersion and their type, as responsible for it. The variations in the osmotic pressure must be explained by the same kind of changes by which we explain, for example, the variations in their internal friction, namely, "changes in state."

The influence of degree of dispersion upon osmotic pressure is very evident in congo red. W. M. Bayliss (*l.c.*) prepared a pure and *highly dispersed* congo red by allowing NaOH to diffuse into its free acid contained in an osmometer.[1] While the free acid is pronouncedly colloid, as betrayed by the fact that it is readily resolved ultramicroscopically, congo red prepared in the manner described, cannot be thus resolved. But it can be as soon as *traces of electrolytes* are added. Even the carbon dioxide of the air suffices to do this. At the same time, the osmotic pressure of the system decreases. All factors which cause a decrease in degree of dispersion, as the addition of electrolytes, ageing, shaking, etc., reduce the osmotic pressure. Other factors which increase the osmotic pressure, as the addition of alkalies, also make the ultramicroscopically heterogeneous structure give way to an optically homogeneous one.

The fact observed by J. Duclaux[2] that the osmotic pressure of a *red* gold hydrosol is considerably greater than that of a *blue* one also belongs here. We have every reason for believing that blue gold sols are not as highly dispersed as red ones.

The view advanced here that changes in the state of a colloid, more especially variations in its degree of dispersion and its type, are of particular significance in determining its osmotic pressure, is perhaps most clearly demonstrated by the close analogies between the osmotic phenomena exhibited by colloids and their internal friction and swelling. The close relationship between these processes is brought out not only by emphasizing that age, previous thermal history and mechanical treatment affect all of them in the same general way, but by the fact that they do this often down to the minutest details. This is clearly apparent when we compare the influence of acids and alkalies on the osmotic pressure (R. S. Lillie) with their effect upon the internal friction (Wo. Pauli, etc.). Still more striking, perhaps, is a comparison of the effects of acids and alkalies on the osmotic pressure of 1.25 percent gelatine solutions (R. S. Lillie) with those of these same substances on the swelling of gelatine discs (Wo. Ostwald).[1] Here the agreement is perfect even to details (see Figs. 58, 59, pp. 251, 252).[2] In connection with these facts the influence of added substances on the viscosity of gelatine solutions, as given on p. 173, should also be studied.

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[1] The similar behavior of freshly prepared silicic acid is discussed on p. 232.

[2] J. Duclaux, Compt. rend., **148**, 295 (1909); for a description of the special method used by this author in determining the osmotic pressure see this paper and Koll.-Zeitschr., **3**, 134 (1908).

As a matter of fact, the relation between osmosis and swelling is close even when the question is viewed from a theoretical standpoint. In the place of a selectively permeable membrane, we have the *structure* of the material undergoing swelling which hinders the movement of the dispersed phase into the dispersion or swelling medium. The process leading to the highest attainable homogeneous (spatial) distribution of swelling substance and swelling producing medium, is possible only if the structure and the specific surface of the swelling body change simultaneously, while the spatial continuity of the two phases to each other remains. If this continuity is destroyed, as by increase of temperature, above a critical value, then instead of swelling, solution occurs. Besides these analogies between the osmosis and the swelling of colloids (as well as between osmotic and swelling pressures), characteristic differences also exist between them. In the process of swelling, a radical change in state, namely, an increase in degree of dispersion takes place. In the osmotic processes of molecularly dispersed systems, the specific surfaces, etc., of the dispersed particles remain constant and only the redispersed substance at 0°, c the concentration (in percent), p the observed osmotic pressure in mm. of Hg., T_1, the observed absolute temperature, and T_0, 273°. Since J. H. van't Hoff first formulated this law the different investigators who have measured the osmotic pressure of colloids have, also, in many cases tried to deduce therefrom their "molecular weight." Indeed, there exist but few publications on the osmotic pressure of colloids in which there is not a column devoted to their "molecular weight" as calculated from the osmotic pressures. Many examples could be given of this.

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[1] Wo. Ostwald, Pflüger's Arch., **108**, 563 (1905).

[2] According to R. S. Lillie the acid minimum is about one-tenth that found by Wo. Ostwald in his experiments on swelling. But since the latter minimum is practically identical with that of the viscosity maximum of dilute gelatine solutions as found by P. von Schroeder (p. 173) and agrees fully with the acid maximum for albumin solutions (see H. Handovsky, Koll.-Zeitschr., **7**, 192, 1910) Lillie's figure evidently represents an error either in measurement or calculation.

The striking thing about these "molecular weights" of colloid systems is their *great absolute value* and their *great variability* under different conditions. The former seems obvious enough in view of the low values found for the osmotic pressure of colloids of even simple chemical composition. The second, however, according to which the molecular weight varies under different circumstances is, strictly speaking, a *contradiction in terms*, for by definition, the molecular weight is a *constant*. But disparities between the molecular weights of substances, as deduced from osmotic measurements and from analysis, have been observed in molecularly dispersed systems also. In other words, the simple proportion between osmotic pressure and concentration, as demanded by theory, has not always been observed to hold even here. Thus W. M. Bayliss (*l.c.*, 1910) cites the fact that the molecular weight of alcohol dissolved in benzene rises from 50 to 208, is quadrupled, in other words, in passing from a concentration of 0.494 percent to one of 14.63 percent. It must be left to the students of the molecularly dispersed solutions to interpret these contradictions between their fundamental equation and its applications. But so far as the colloids are concerned, such a calculation of molecular weight from osmotic measurements can never be attempted with safety because it is wrong in principle. *Not even the sense of the variations in the osmotic pressure of colloid solutions and their concentration need be the same in all cases.* On p. 245 it was pointed out that, according to J. Duclaux, the osmotic pressure of iron hydroxide sol increases more rapidly than its concentration. Thus, while we generally observe an increase in the molecular weight with increasing concentration, due to the relatively smaller increase in the osmotic pressure, in the example just quoted we observe a decrease in molecular weight, even to one-tenth the original. The "molecular weights" of acid and alkali albumin would even be found to yield complicated curves with maxima and minima related to the concentration of the added electrolytes. In fact, two or three entirely different concentrations of acid or alkali would be found in which the molecular weights of the albumin, or its combination with an electrolyte, would be the same, thereby contrasting with the molecular weights observed in all other concentrations. Similarly, salts would affect the "molecular weight," making it either rise or fall, depending solely upon the concentration of the added electrolyte. Depending upon the acid or alkaline reaction of the colloid, the "molecular weight" of a colloid might be *either* raised or lowered on adding a salt. With rising temperature, the molecular weight of some colloids would be increased, of others decreased. The "molecular weight" of a colloid would be changed by shaking or stirring, by ageing and by being warmed either slowly or rapidly. These illustrations will suffice to demonstrate the impropriety of applying the ordinary concept of "molecular weight" to colloid solutions.[1] It is hard to see how a "constant" which varies between several hundred and infinity with concentration alone, as in soap solutions, can be of any value in the physico-chemical characterization of a system.

In this condemnation of the value of "molecular weight" determinations of colloidally dissolved substances by osmotic methods,[2] it is not maintained that there may not exist *transition systems* between colloidally and molecularly dispersed systems in which there is at least an approximate proportionality between osmotic pressure and *concentration*, and therefore a proper basis for the calculation of the molecular weight. In fact, W. M. Bayliss (*l.c.*) discovered such a system in congo red, freshly prepared by the method described above (see also W. Biltz and A. von Vegesack, *l.c.*). This dye when fresh and free from electrolytes, is highly dispersed, as evidenced by its ultramicroscopic properties, its considerable osmotic pressure, etc. In this *pure* condition a 0.465 percent solution yields an osmotic pressure of 60 mm. of water. If now, by the formula given above, the molecular weight of the pure congo red is calculated, the answer is a value of 90 to 95 percent of that obtained by analytical methods (696.47). W. Biltz and F. Pfenning obtained similar results. This shows that pure congo red behaves like a typical molecular dispersoid, at least in its osmotic relations. The applicability of the above formula to the determination of the molecular weight of this dye is also evidenced by the direct proportionality existing between concentration and pressure, in other words, the constancy of the quotient $\frac{p}{C}$, as evidenced in Table 49, on p. 244. In cases of this type, and *only* in such, are molecular weight determinations by this method justified. Moreover, the considerable electrical conductivity of pure congo red solutions as studied by W. Biltz and A. von Vegesack further shows that we deal in this case with a molecular dispersoid rather than with a colloid, for high conductivity is not characteristic of typical colloids.

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[1] See in this connection J. Duclaux, Compt. rend., **148**, 714 (1909).

[2] For the determination of the "molecular weight" of colloids by indirect methods, as by measuring the vapor tension, the boiling or freezing points, etc., see p. 142.

9. On the Moleculo-kinetic Theory of Osmosis in Colloid Systems.—In view of the successful applications that have been made of moleculo-kinetic conceptions to the quantitative study of the phenomena of movement exhibited in colloid systems, it may be asked if they may not also be of service in the theory of the osmotic pressure of these systems. A. Einstein and M. von Smoluchowski[1] have considered this question. They conclude that the *osmotic pressures of two equally concentrated but differently dispersed phases are inversely proportional to the cubes of the radii of their particles.*[2] In other words,

$$\frac{P_1}{P_2} = \frac{(r_2)^3}{(r_1)^3}$$

This highly interesting conclusion has not yet been tested experimentally.

It is of interest that the above conclusion was reached on the basis of considerations in which it was assumed that the Boyle-Gay-Lussac law (direct proportion between pressure and concentration as well as absolute temperature) was valid. This assumption holds, of course, only at great dilutions. The Svedberg[1] tried to determine *indirectly* the validity of the Boyle-Gay-Lussac law for colloids. An equation governing *local changes in the motion of particles showing Brownian movement, so far as extent and frequency are concerned*, may be derived from the equation of von Smoluchowski (*l.c.*). A detailed exposition of this second equation and the considerations leading to it cannot be given here. The Svedberg, however, found highly diluted gold and mercury sols to obey it. He concluded, therefore, that the Boyle-Gay-Lussac law used in deriving the formula would also have to be valid for greatly diluted colloid systems. It is perhaps too early to concur entirely in this conclusion, since the number of mathematical assumptions in the formula is exceedingly great. Besides, Svedberg's figures (see especially their graphic representation on p. 555 of his paper, *l.c.*, 1910) themselves show that the law holds strictly only at a transition point, for only in very dilute concentrations is there strict agreement between observation and theory. Deviations from the rule, and therefore from the Boyle-Gay-Lussac law, begin to appear in the case of a mercury sol as soon as its concentration amounts to $\frac{1}{6}.10^{-10}$ normal, or about 0.000,000,000,3 percent by weight. In view of the slight *practical* significance of the concentration range over which it is valid, the law appears to be an ingenious theoretical deduction rather than a means of studying quantitatively the dependence of osmotic pressure in colloid systems on concentration and temperature.

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[1] M. von Smoluchowski, Boltzmann-Festschrift, 626, Leipzig, 1904.

[2] See The Svedberg, van Bemmelen-Gedenkboek, 131, 1910.

Addendum: Other Types of Movement in Dispersoids

The phenomena of movement observed in colloid systems under the influence of an *electric current* will be discussed at another time. At this point we merely wish to mention the phenomena of movement which occur under the directive influence of *heat* and *light*. The botanists F. Stahl[2] and W. Sachs[3] observed such directed movements in small solid and liquid particles while attempting in 1876 to determine to what extent the thermal and heliotropic movements of unicellular organisms (such as zoospores) depended upon biological properties and in how far they were merely passive. The directive influence of light on the movement of dispersed particles was later studied in detail by G. Quincke.[1] W. R. Whitney and C. J. Blake[2] have studied such light and heat effects on the movement of colloid particles in colloid gold. The *directive influence of light on crystallization and sublimation* should also be mentioned here.[3]

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[1] The Svedberg (*l.c.*), as well as Zeitschr. f. physik. Chem., **73**, 547 (1910).

[2] F. Stahl, Bot. Ztg., 715 (1876); Verh. d. phys.-med. Ges. Wurzburg, **14** (1879).

[3] W. Sachs, Flora, 241 (1876). See also E. Strassburger, Jenaisch. Z. f. Naturw., 12 (1878).

§31. Filtration and Ultrafiltration of Colloid Systems

1. Filtration of Colloid Systems.—A property which distinguishes colloid solutions from coarse suspensions is the ability of the former to pass unchanged through filter paper. It is by this means that we recognize the formation of a colloid solution when we wash a precipitate with pure water. While typical colloids pass through *all* filter papers, somewhat coarser systems begin to be held back by hardened filter papers and by clay and porcelain filters as those of Berkefeld, Reichel, Chamberland and Pukall.

The filtrability of a dispersoid depends upon the size, shape and rigidity of its particles, upon the filtration pressure and the nature of the filter, more especially the size of its pores.[4] To determine the approximate size of the dispersed particles it is therefore well to know the average size of the pores of different filters. Such determinations, as made by H. Bechhold,[5] are given in Table 60.

Table 60.—Size of Pores in Filters
(According to H. Bechhold)

Filter	Average size of pores (permeability to water)	Size of largest pores (permeability to air)
Ordinary thick filter paper	3.3μ	
Filter paper No. 556 (Schleicher and Schüll)	1.7μ	
Filter paper No. 602 (extra hard, Schleicher and Schüll).	0.89–1.3μ	1–1.5μ
Chamberland filter		0.23–0.41μ
Reichel filter		0.16–0.175μ

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[1] G. Quincke, Report Brit. Assoc. Advanc. Science, Glasgow, 60 (1901); Drude's Ann. d. Physik., **7**, 701 (902).

[2] W. R. Whitney and C. J. Blake, Journ. Amer. Chem. Soc., **26**, 1347 (1904).

[3] See the summary of J. M. Eder, Photochemie, 3 Aufl., 123, Halle, 1906.

[4] Details regarding this question may be found in the paper of E. Hatschek, J. Soc. Chem. Industry, **27**, 538 (1908); also Koll.-Zeitschr., **6**, 254 (1910); **7**, 81 (1910).

[5] H. Bechhold, Zeitschr. f. physik. Chem., **64**, 328 (198).

The original paper must be consulted for details of the methods used by Bechhold in arriving at the assigned values.

As the table shows, typical colloids, with particles having a diameter of less than 0.1μ, must be just able to pass through the filter lowest in the list. But even with pores of this size by-effects, known as "adsorption" effects, often appear, due to the action of the filter itself upon the dispersed phase. These lead to retention of the dispersed phase and so to a clogging of the pores of the filter. At other times coagulation processes occur due to this surface action. Whenever any of these things take place, filtration cannot, of course, any longer tell us anything definite regarding the size of particles in a dispersoid.

2. Ultrafiltration of Colloid Systems.—After W. Schmidt[1] and F. Hoppe-Seyler[2] had found that solutions of albumin and of gum became more dilute by being filtered through animal membranes, C. J. Martin[3] discovered that colloidally dissolved materials could be completely separated from their dispersion medium by being filtered through organic or inorganic gels. To give these a proper support he used Chamberland filters and impregnated them with gelatine or silicic acid. He could then filter liquids under 30 to 100 atmospheres of air pressure without breaking the filter. By using this method, he was able to separate from the albumin a clear fluid containing salt but entirely free of protein. Table 61 contains the more important of his results.

Such filtration through gels was next used by French investigators (Borrel and Manea, 1904; G. Malfitano, 1904; J. Duclaux, 1905)[4] to separate the dispersed phase from the dispersion medium in different organic and inorganic colloids. They usually employed collodion thimbles as filters.

H. Bechhold[5] took an important step forward in this problem of filtration when in 1906 he discovered the *permeability of gels to be a function of their concentration*. He found dilute gels to be more permeable than more concentrated ones. For details regarding his methods his original publications must be consulted. As a rule, he used ordinary filter papers as a foundation, impreg-

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[1] W. Schmidt, Poggendorf's Ann., 337 (1856).

[2] F. Hoppe-Seyler, Virchow's Arch., **9**, 245 (1861).

[3] C. J. Martin, Journ. Physiol., **20**, 364 (1896); see also E. W. Reid, *ibid.*, **27**, 161 (1903); A. Craw, Zeitschr. f. physik. Chem., **52**, 569 (1898); Proc. Roy. Soc., **77**, 172, 311 (1899).

[4] For the history of filtration through gels see J. Duclaux, Koll.-Zeitschr., **3**, 134 (1908); also H. Bechhold, *ibid.*, **3**, 226 (1908).

[5] H. Bechhold, Z. f. Elektroch., **12**, 777 (1906); Koll.-Zeitschr., **1**, 107 (1906); **2**, 3 (1907); Zeitschr. f. physik. Chem., **60**, 237 (1907); **64**, 328 (1908).

TABLE 61.—FILTRATION THROUGH CLAY CELLS IMPREGNATED WITH SILICIC ACID
(According to C. J. Martin)

Impermeable to	Partially permeable to	Readily permeable to
Egg albumin.	Alkali albumin.	All albumoses.
Serum albumin.	Acid albumin.	Urochrome (pigment of urine).
Egg globulin.	Caramel.	All crystalloids.
Serum globulin.	Biliverdin (bile pigment).	
Fibrinogen.	Dextrin.	
Caseinogen.		
Nucleoalbumin.		
Hemoglobin.		
Glycogen.		
Soluble starch.		
Soluble starch (amylodextrin)		

TABLE 62.—ULTRAFILTRATION
(According to H. Bechhold)

Dispersoid	The disperse phase is held back by a gelatine gel of the following concentration in percent	Remarks
Platinum sol (Bredig)	2	Average size of particles about $44\mu\mu$ (Zsigmondy).
Colloid iron hydroxide	2	
Casein (of milk)	2.5	
Colloid gold containing sodium lysalbinate (Zsigmondy).	3	About $40\mu\mu$.
Collargol (v. Heiden)	3.5	About $20\mu\mu$.
1 percent hemoglobin solution.	4	
1 percent gelatine solution	4	
Serum albumin	4-4.5	Molecular weight—15,000 down to 3000.
Protalbumoses		
Silicic acid	4.5	
Deutero-albumoses *A*	8	Molecular weight about 2400.
Deutero-albumoses *B* and *C*.	10	Traces pass through.
Dextrin	10	Small amounts pass through; molecular weight about 965.
All crystalloids	....	Pass through.

nating them with various gels, as acetic acid-collodion, gelatine-formaldehyde, etc. Table 62 gives a survey of his results.

It is evident that the filter becomes less permeable as the concentration of the gel rises. A hardened 10 percent gelatine filter holds back even molecules of the size of those contained in dextrin. A proper series of filters makes it possible to distinguish, within the range of colloid dispersion, between systems of different degrees of dispersion, and these are then found to correspond with a differentiation between them made on optical grounds. For this reason H. Bechhold has named his method "*Ultrafiltration*."

Recently A. Schoep[1] has described a simple method of ultrafiltration, in which is eliminated the disadvantage of having to work with high pressures.[2] He found that filters of different degrees of permeability could easily be made by adding to collodion solutions different amounts of glycerine and castor oil. Dialyzing thimbles may be made from such mixtures by the methods described in the practical introduction on p. 10. The dry collodion thimbles become progressively more permeable (within certain limits) as the amount of glycerine or castor oil in them is increased. Fig. 63 illustrates Schoep's simple method.

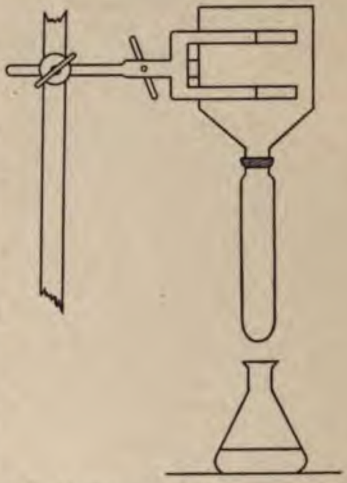

FIG. 63.—*A. Schoep's* arrangement for ultrafiltration.

We cannot advantageously discuss the theory of this variable permeability of gels of different concentrations until we have treated their general structure.

In conclusion, it must be mentioned that undesirable by-effects, such as adsorption of the disperse phase by the filter, occur in ultrafiltration, also. Ultrafiltration yields dependable results, therefore, only if checked up by other methods.

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[1] A. Schoep, Bull. Soc. Chim. Belg., **24**, 354 (1910); Koll.-Zeitschr., **8** (1911). See also A. von Lebedew, Zentralbl. f. Physiol., **23**, 767; **24**, 511 (1910).

[2] Emulsoids may be separated from their dispersion medium, with Schoep's filter, only when pressure is used.

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